Primary and Secondary Lithium Batteries Capable of Operating at Low Temperatures for Planetary Exploration

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Outline

- Introduction
- Potential Applications of Low Temperature Batteries
- Low Temperature Rechargeable Li-ion Batteries
- Low Temperature Lithium Primary Batteries
- Low Temperature Supercapacitors
- Conclusions
- Future Development

Low Temperature Li-Ion Batteries

- **NASA desires Li-ion batteries than can operate over a wide temperature range for future planetary lander and rover applications** ***(i.e., -60 to +30^{o}C).***
- **DOE desires Li-ion batteries than can operate over a wide temperature range** ***(i.e., -30 to +60^{o}C).*** **and provide good life characteristics for HEV and PHEV applications**

Objectives and Approach

- ***Develop advanced Li-ion electrolytes that enable cell operation over a wide temperature range (i.e., -60 to +60^{o}C).***
- **Improve the high temperature stability and lifetime characteristics of wide operating temperature electrolytes.**
- **Define the performance limitations at low and high temperature extremes, as well as, life limiting processes.**
- **Demonstrate the performance of advanced electrolytes in large capacity prototype cells.**

Li-Ion Battery- A Preferred Solution over SOA

- Significant enhancement in the mission with 4X improvement in mass and ~ 8X enhancement in volume compared Ni-Cd and Ni-H_2.
- Enables missions (Mars and Lunar) due to wide range of operating temperatures, especially at low temperatures down to -40^{o}C, due to the of non-aqueous electrolyte solutions.
  - Some of the recent electrolyte formulations extend this range to -60^{o}C.
- Excellent coulombic and energy efficiency (reduced radiator)
- No compromise on cycle life comparable to nickel systems
  - About 30,000 cycles demonstrated at partial DOD .
- Calendar life as good as with nickel systems
  - Over six years demonstrated in real-time tests.
  - Tolerance to high intensity radiations,
  - Demonstrated to over 16 MRad cumulative radiation.
- Reduced maintenance (reconditioning)
  - No memory effect (low voltage plateau)
- Safety, especially in human exploration missions
  - Safety demonstrated in robotic missions, with charge control electronics, when needed. Human-rated safety yet to be demonstrated.

Why Battery Performance Degrades at Low Temperatures?

- Increased cell polarizations in general
  - Ohmic, kinetic as well as mass transfer
- Increased Ohmic polarization
  - Mainly contributed by the electrolyte
    - Reduced Ionic mobility in electrolyte.
      - Slow diffusion of ions mainly due to increased viscosity of solvent components
    - Reduced ionic strength due to lower solubility at low temperatures.
- Slower electrode kinetics
  - Slower charge transfer at the electrodes governed by Arrhenius dependence.
  - Charge-transfer over film-covered electrodes?
- Enhanced mass transfer polarization
  - Slow diffusion of (Li^+) ion in solution caused by increased electrolyte viscosity
  - Slower diffusion of reactant/product species in the electrode lattices (bulk diffusion).
  - Surface films complicating the charge transfer process.

Low Temperature Lithium Ion Electrolytes

Electrolyte Development: Approach/Background

Factors Affecting the Low temperature Performance of Li-Ion Batteries

- **Cell Design Features**
  - Separator Material Properties
  - Current Collection (Tabing)
  - Cell Size and Thermal Properties
- **Electrolyte Properties**
  - Electrolyte Conductivity
  - Electrode Passivation
- **Electrode Properties**
  - Active Material Loading
  - Bulk Li^+ Diffusion
  - Li^+ Kinetics (Diffusion in SEI)

- ***Of these factors, the electrolyte properties have the most dramatic impact on low temperature performance (i,e., if the the electrolyte is frozen the cell/battery will not operate).***
- ***Sufficient electrolyte conductivity at low temperature is not sufficient to ensure efficient operation due to potential reactivity leading to poor kinetics and/or inadequate life aspects.***
- ***To enable very low temperature operation (< - 40°C), high diffusivity electrode materials must be identified coupled with improved cell design.***

Wide Operating Temperature Range Lithium Ion Electrolytes
Electrolyte Development: Approach/Background

- ***Electrolyte Selection Criteria***
  - High conductivity over a wide range of temperatures
    - 1 mS cm-1 from –60 to 40^{o}C
  - Wide liquid range (low melting point)
    - -60 to 75^{o}C
  - Good electrochemical stability
    - Stability over wide voltage window (0 to 4.5V)
    - Minimal oxidative degradation of solvents/salts
  - Good chemical stability
  - Good compatibility with chosen electrode couple
    - Good SEI characteristics on electrode
    - Facile lithium intercalation/de-intercalation kinetics
  - Good thermal stability
  - Good low temperature performance throughout life of cell
    - Good resilience to high temperature exposure
    - Minimal impedance build-up with cycling and/or storage

- ***In addition to meeting these criteria, the electrolyte solutions should be ideally have low flammability and be non-toxic !!***

Low Temperature Lithium Ion Cells and Batteries

Performance Summary of Advanced Low Temperature Li-Ion Electrolytes Developed at JPL

Electrolyte Type	- 20°C Enabling 1.0M $LiPF_6$ EC+DEC+DMC (1:1:1 v/v %) GEN 1 ('96-'00)	- 40°C Enabling 1.0M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:2 v/v %) GEN 2 ('97-'01)	- 50°C Enabling 1.0M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v %) and Ester-Based GEN 3 ('00-'03)	- 80°C Enabling Ester-Based (i.e. 1.0M $LiPF_6$ EC+EMC+MB (1:1:8 v/v %) GEN 4 ('04-'05)
Operating Temperature at C/5	- 20 to + 40°C	- 40 to +40°C	-60 to + 40°C	-80 to + 25 C **(Goals)**
Specific Energy (Wh/kg)				
25 C	125	125	125	125
-20 C	75	95	105	110
-40 C	< 40	75	85	90
-60 C	NA	NA	50-65	70
-80 C	NA	NA	NA	50
100 % DOD Cycle Life	>1500	>1500	>1500	TBD
NASA Application	MSP 2001 Lander MER 2003 Rover Phoenix 2007 Lander MSL 2011 Lander	Future Mars Landers and Rovers	Future Mars Landers and Rovers	Future Mars Surface Operations

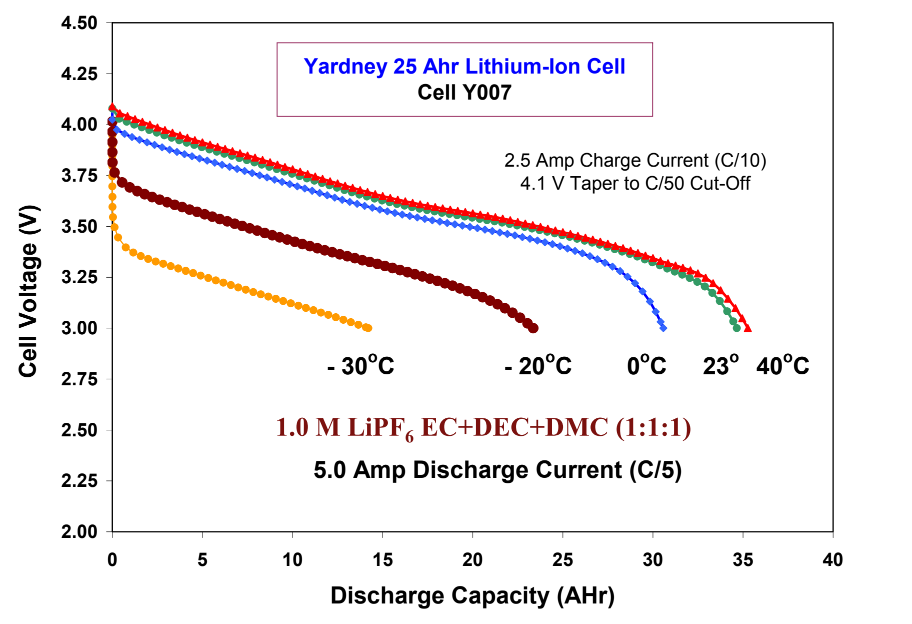
Specific energy values dependent upon prototype cell type and size

Low Temperature Performance of Ternary Carbonate-Based Electrolytes

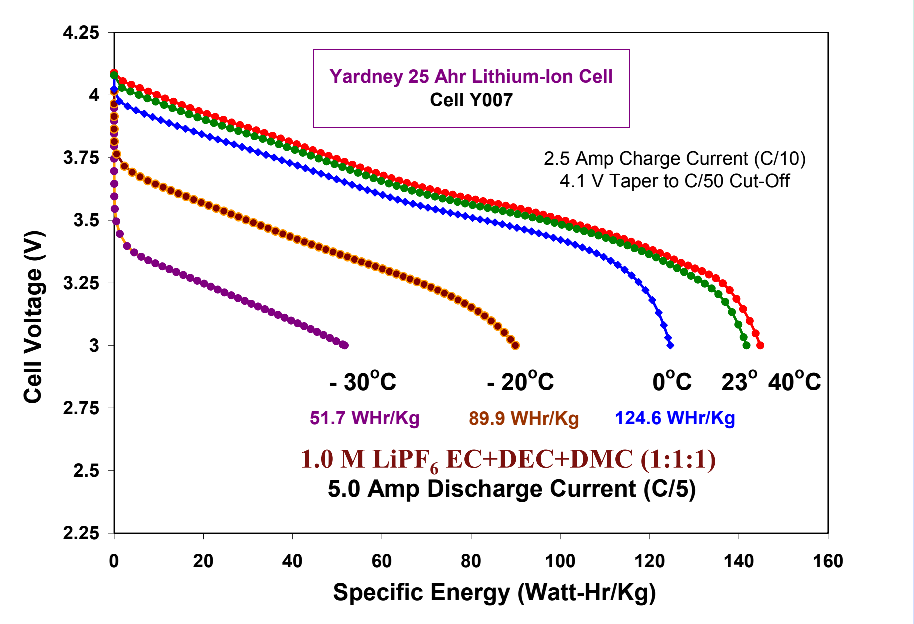
Discharge Capacity at Various Temperatures

Performance in Lithion (Yardney) MSP01 Design Prototype Cells

Discharge Capacity (AHr)



Discharge Energy (WHr/Kg)



- Cell charged at respective temperature prior to discharge (C/10)
- Improved low temperature performance observed with room temp. charge

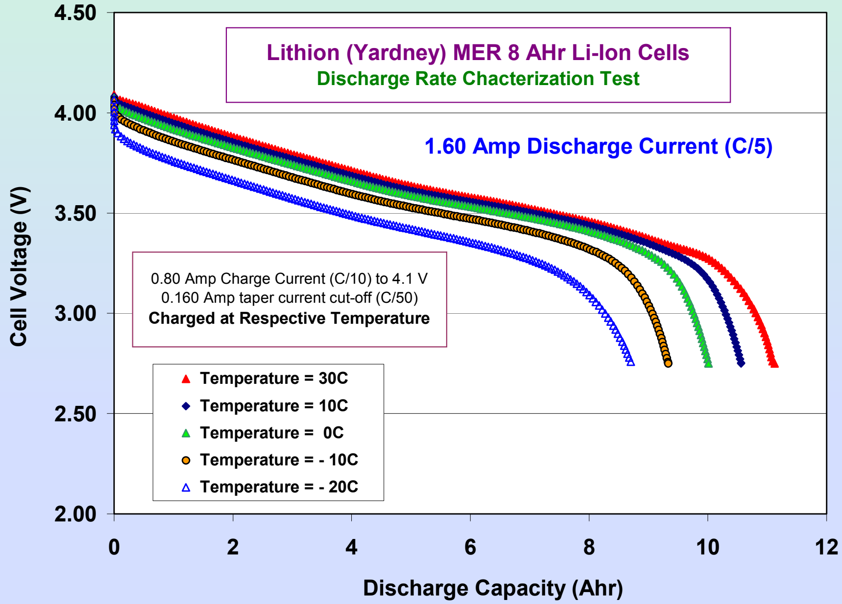
M. C. Smart, B. V. Ratnakumar, L. Whitcanack, S. Surampudi, L. Lowry, R. Gitzendanner, C. Marsh, F. Puglia, J. Byers, and R. Marsh, 35th Intersociety Energy Conversion Engineering Conference (IECEC), Las Vegas, NV, July 24-28, 2000,

Lithion 8 Ah Li-Ion Cells for Mars Exploration Rover (MER)

Discharge Rate Characterization at Various Temperatures

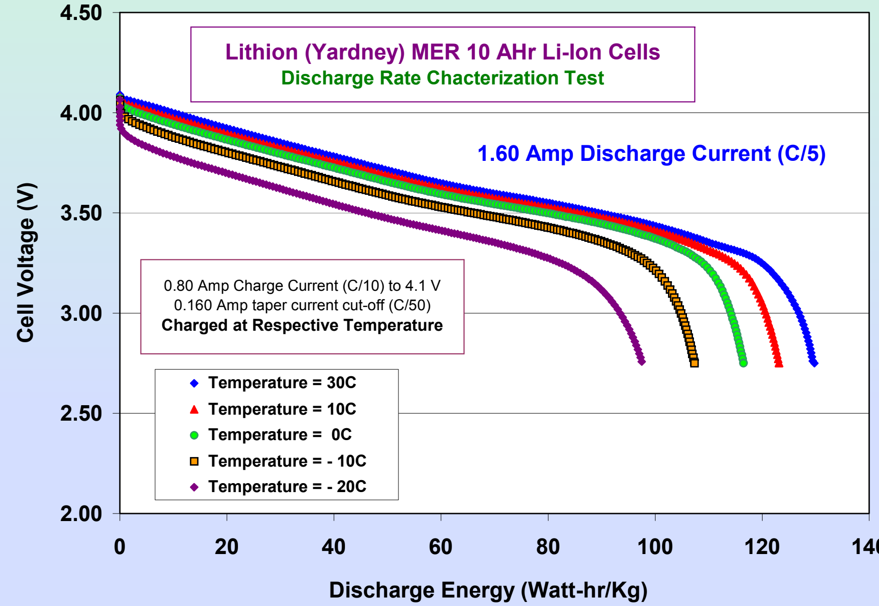
(C/5 Discharge Rate = 1.60 Amps)

Discharge Capacity (Ah)



	Capacity (AHr)	% of RT
30 C	11.122	100.00
10 C	10.561	94.95
0 C	10.012	90.01
-10 C	9.332	83.91
-20 C	8.700	78.22

Discharge Energy (Wh/kg)

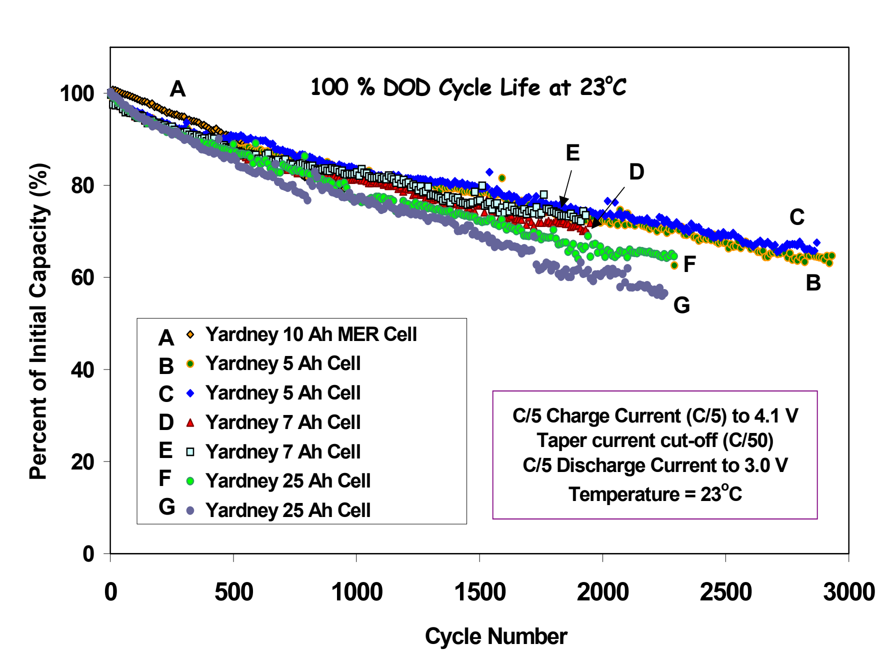


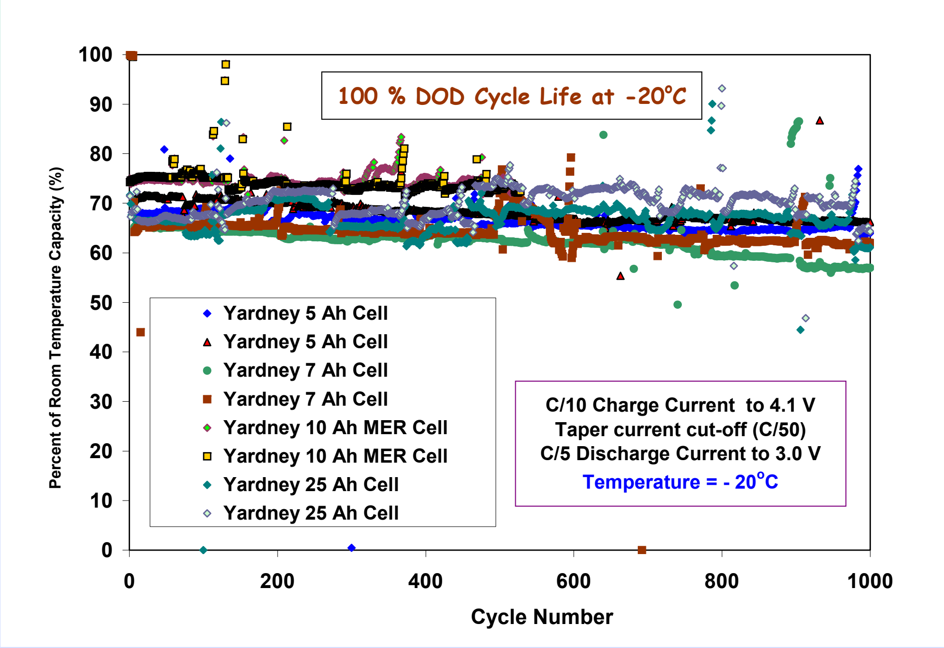
	Energy (WHr/Kg)	% of RT
30 C	129.77	100.00
10 C	123.61	95.25
0 C	116.50	89.77
-10 C	107.35	82.72
-20 C	97.50	75.13

Cells contain 1.0M $LiPF_6$ +EC+DMC+DEC (1:1:1) (Range of operation –30 to +40°C)

Performance Testing of Prototype Yardney Lithium-Ion Cells
100% DOD Cycle Life Performance

Temp = 23°C **Temp = - 20°C**





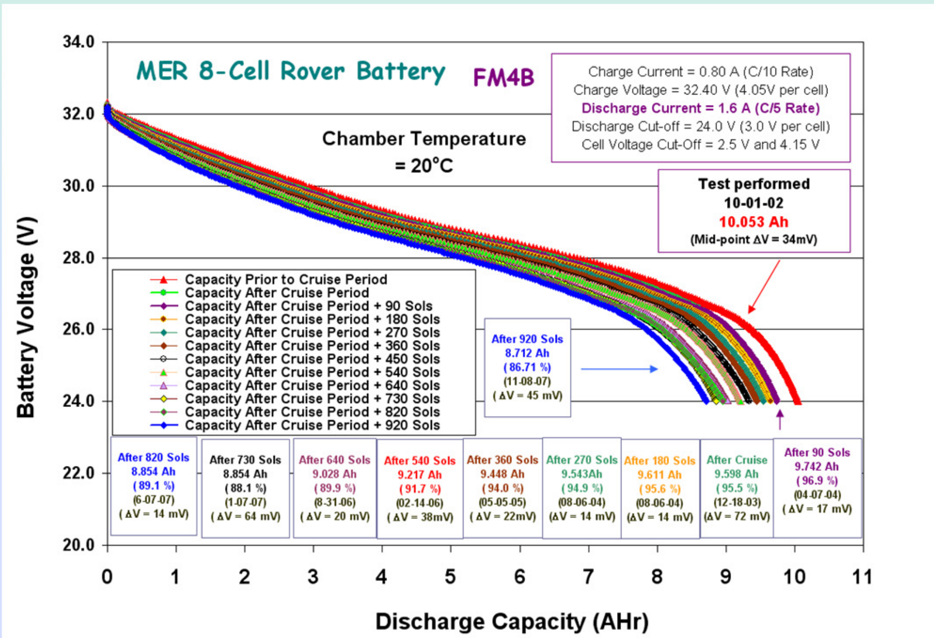
- Comparable cycle life performance obtained with a range of cell sizes fabricated by Lithion, Inc. (from 5 to 25 Ahr).
- Stable performance displayed when continuous cycling is performed at – 20°C (lower capacity fade rate compared to room temperature).

MER 8 Ah Rover Lithium-Ion Battery (FM4B)

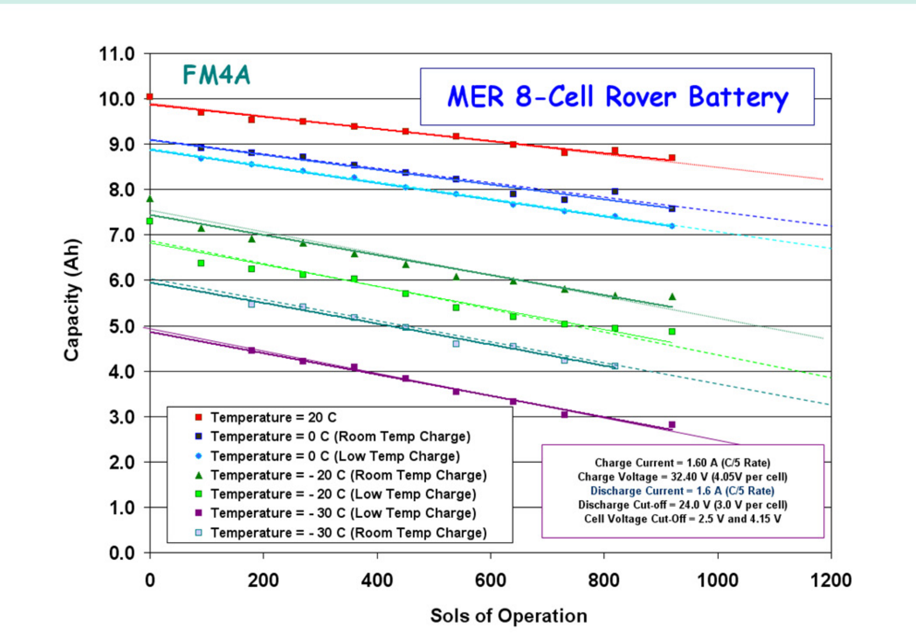
Characterization After Cruise Period + 920 Sols (Mission Simulation Battery)

Observed Capacity Loss After Completing Cruise + 920 Sols

Capacity Determination at 20°C



Capacity Fade Trends



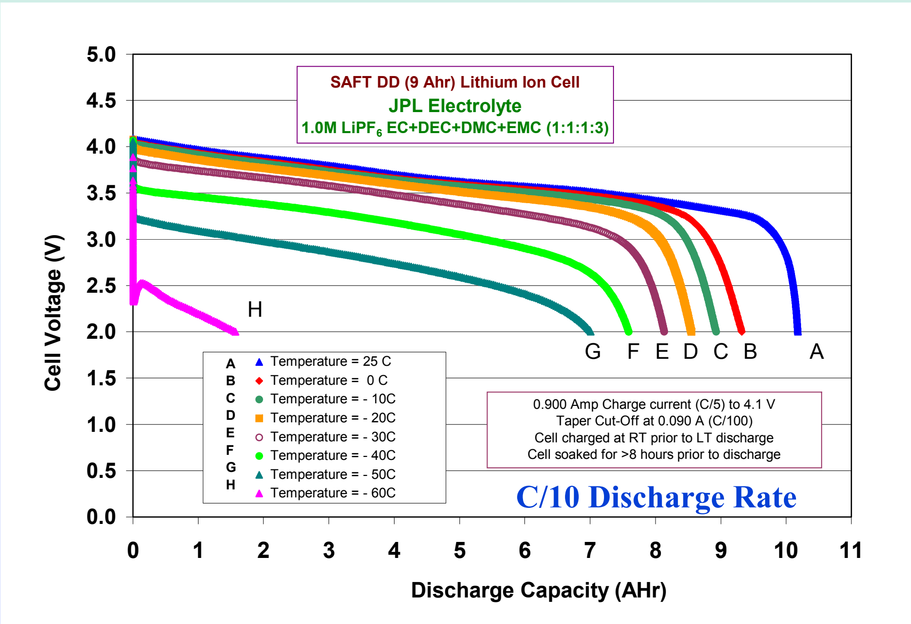
- Approx. 13% capacity loss observed at 20°C since initiation of testing (> 4.00 years).
- **Capacity fade observed to be much more dramatic at low temperature**

M. C. Smart, B. V. Ratanakumar, L. D. Whitcanack, F. J. Puglia, S. Santee, and R. Gitzendanner,
"Life Verification of Large Capacity Yardney Li-ion Cells and Batteries in Support of NASA Missions",
Int. J. Energy Res, **34**,116-134 (2010).

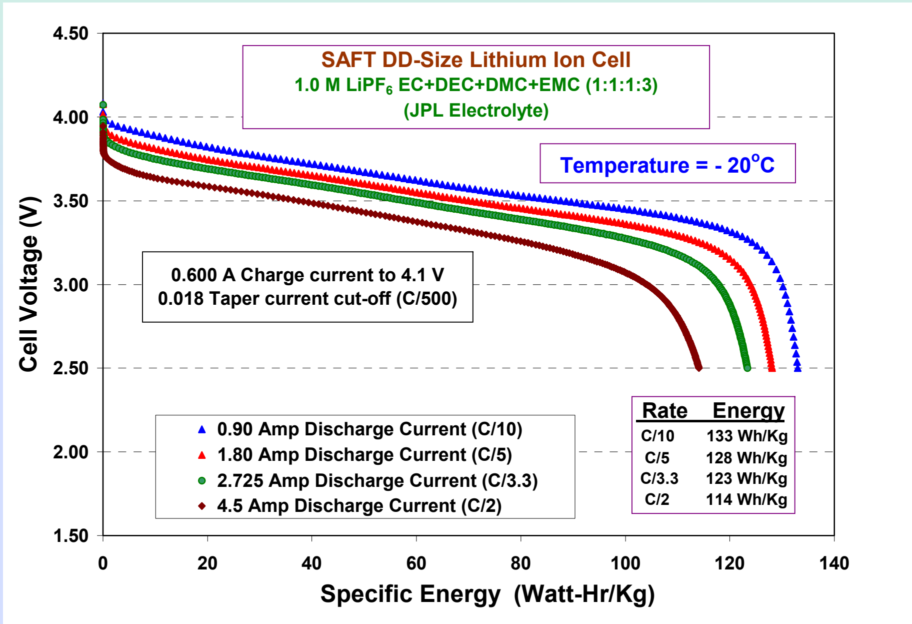
Performance Testing of SAFT DD-Size Lithium-Ion Cells

Cell Performance at Low Temperatures: JPL Electrolyte

Discharge Capacity (C/10 Rate)



Rate Capability at -20°C

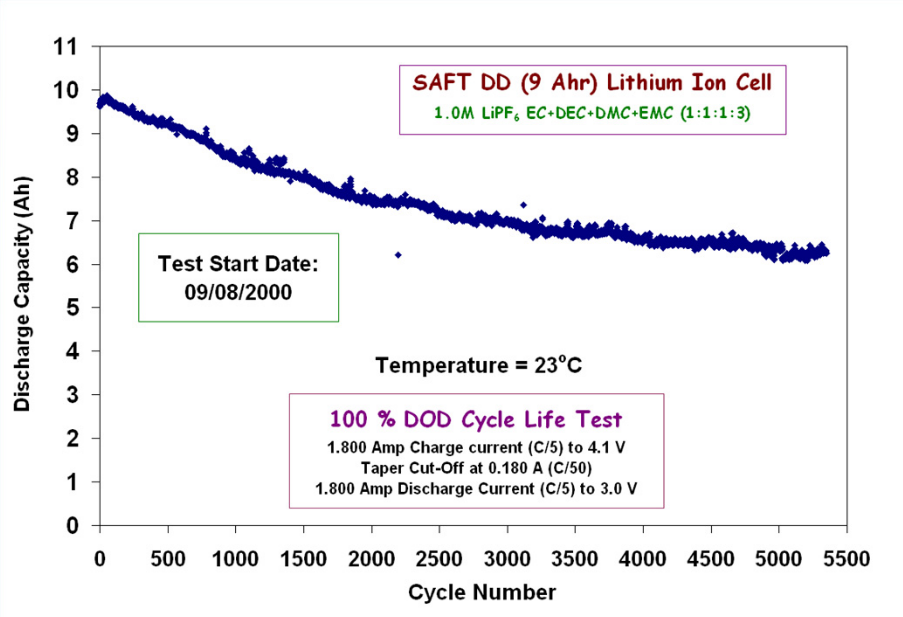


M. C. Smart, B. V. Ratnakumar, L. Whitcanack, K. Chin, and S. Surampudi, H. Croft, D. Tice and R. Staniewicz, "Improved Low Temperature Performance of Lithium Ion Cells with Quaternary Carbonate-Based Electrolytes", *J. Power Sources*, **119-12**, 349-358 (2003).

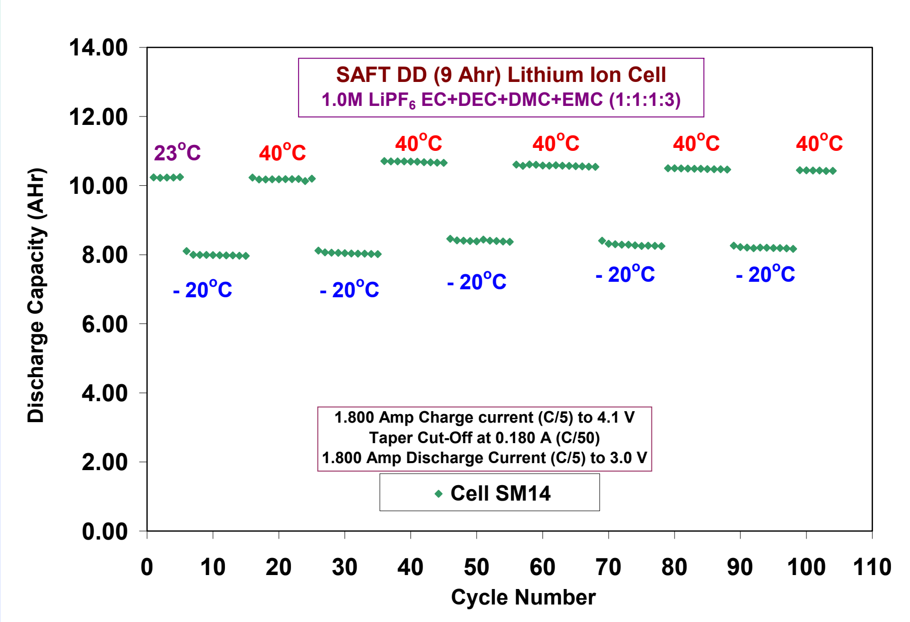
Performance Testing of SAFT DD-Size Lithium-Ion Cells

Prototype cells containing low temperature electrolytes

100% DOD Cycle Life Performance



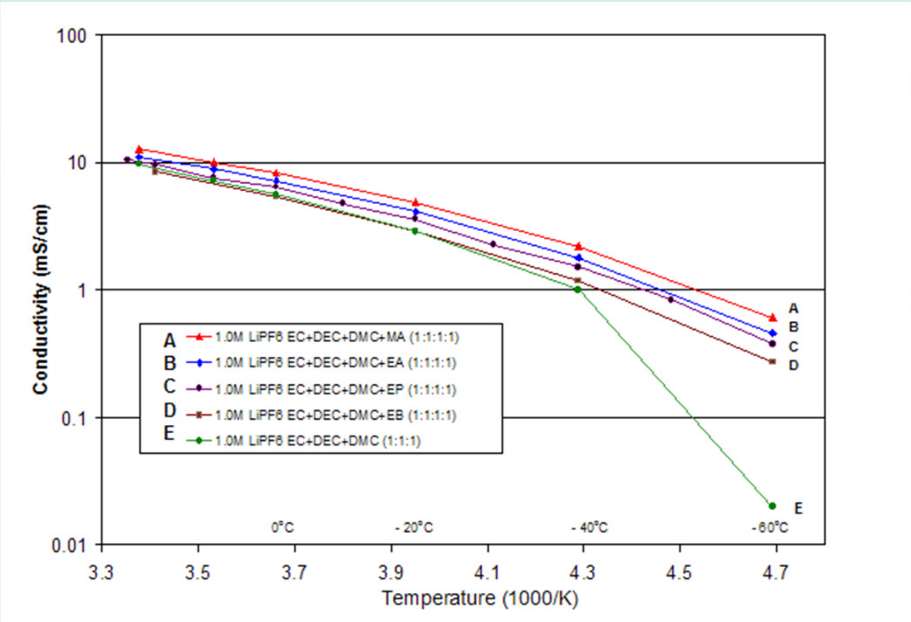
Variable Temperature Cycling

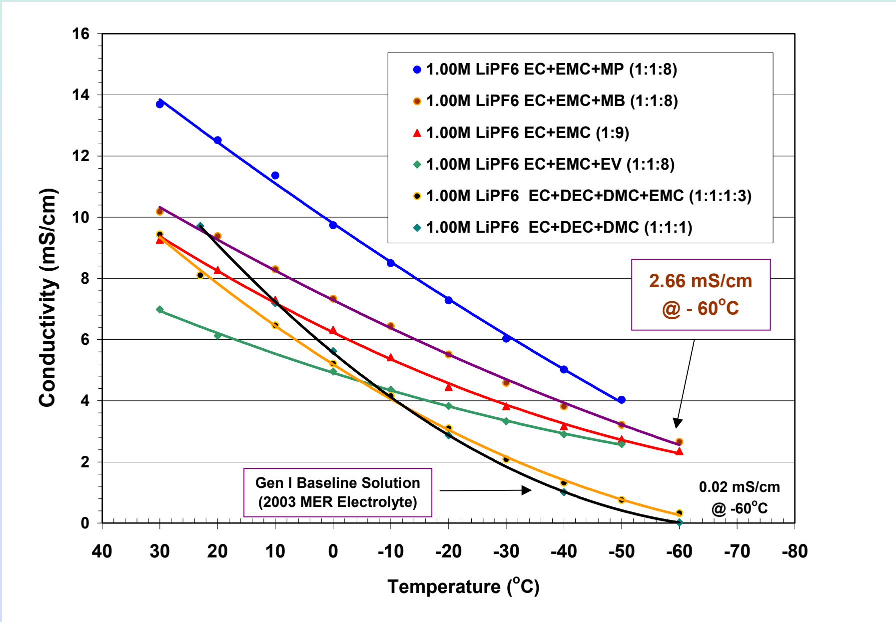


- Cell has been on test over 6 years !!
- Cell contains low EC-content electrolytes.
- Cells have been demonstrated to provide good low temperature performance (e.g., over 90 Wh/kg delivered at -40°C with a C/10 discharge rate)

Ester-Based Electrolytes for Ultra-Low Temperature Li-Ion Batteries

- **Conductivity measurements were performed on a number of electrolytes over a wide temperature range (25 to –70°C)**



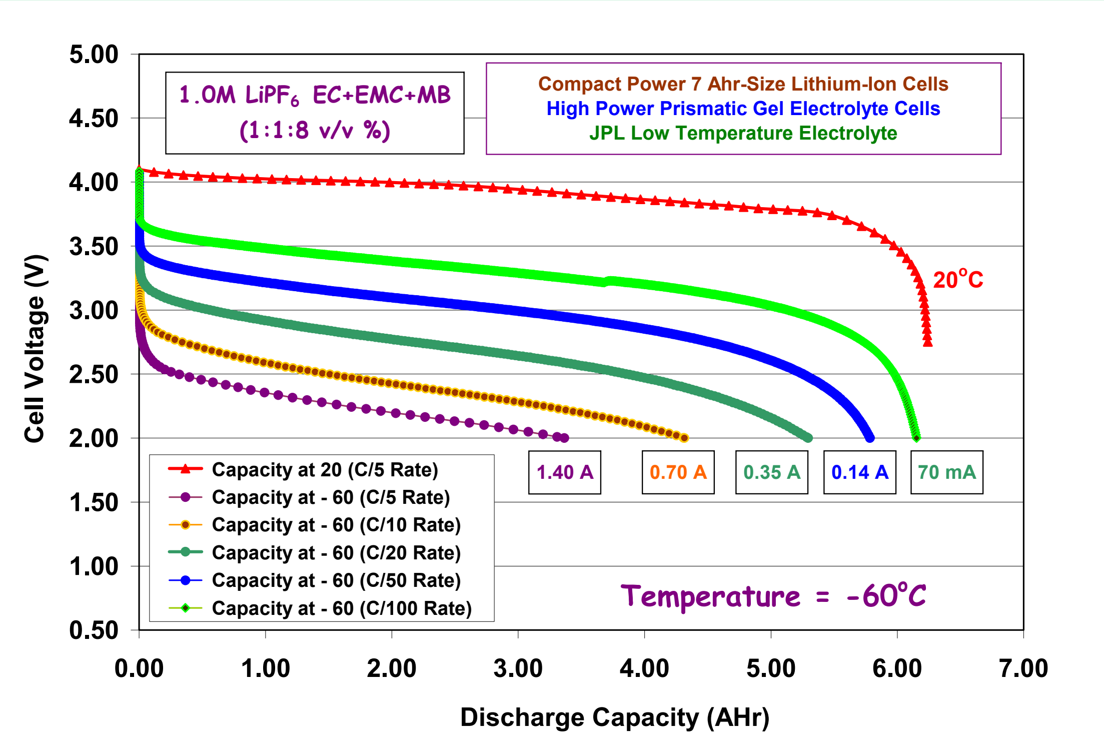


Demonstrated over 2 mS/cm^{-1} at –60°C with methyl propionate (MP)-based and methyl butyrate (MB)-based low temperature electrolytes.

Performance Testing of High Rate, Gel Polymer Electrolyte Li-Ion Cells

Performance of Ester-Based Electrolytes at Low Temperatures

Discharge Performance at –60^{o}C (MB-Based Electrolyte)



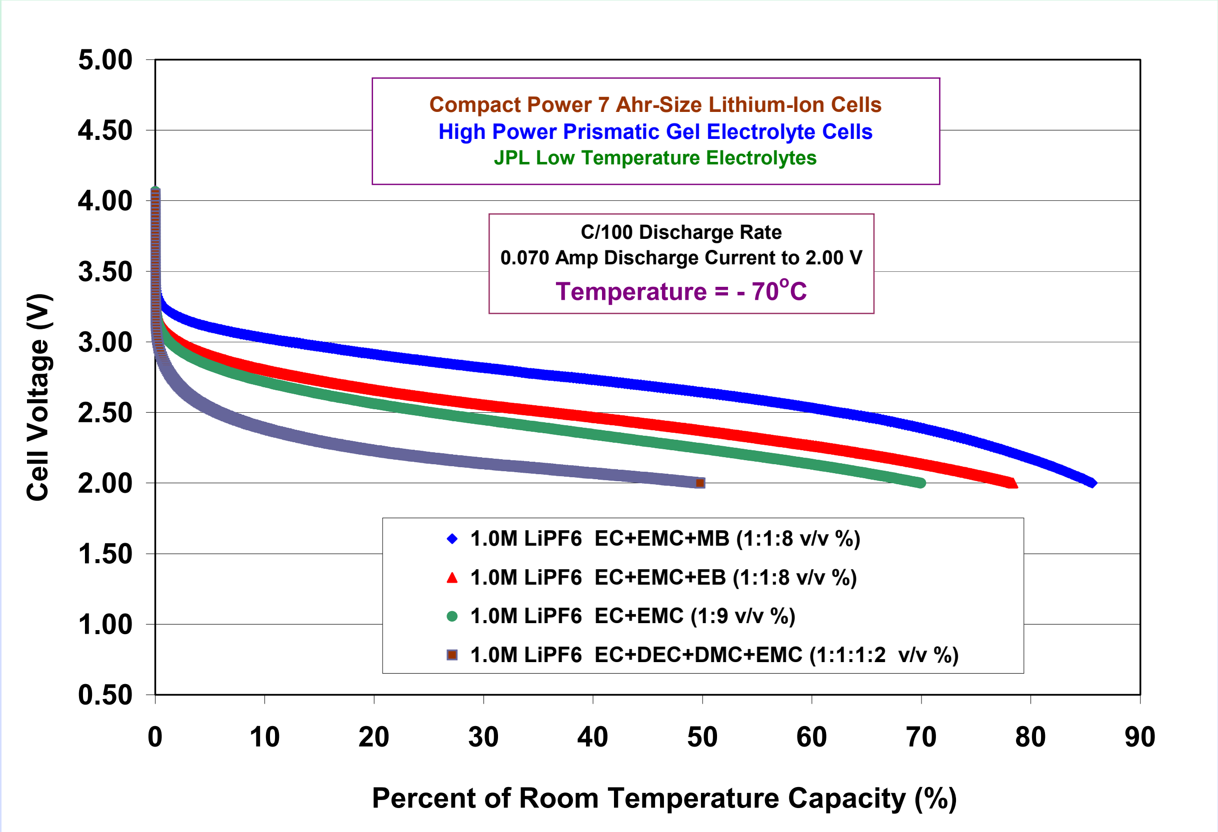
Nearly full capacity was delivered with the methyl-butyrate (MB)-containing electrolyte at –60^{o}C using low rates (C/100) and still delivered ~ 85% of the room temperature capacity using higher rates (C/20).

M. C. Smart, B. V. Ratnakumar, A. Behar, L.D. Whitcanack, J.-S. Yu, M. Alamgir, "Gel Polymer Electrolyte Lithium-Ion Cells with Improved Low Temperature Performance", *J. Power Sources*, **165 (2)**, 535-543 (2007).

Performance Testing of High Rate, Gel Polymer Electrolyte Li-Ion Cells

Performance of Ester-Based Electrolytes at Low Temperatures

Discharge Performance at –70°C (C/100 Rate)



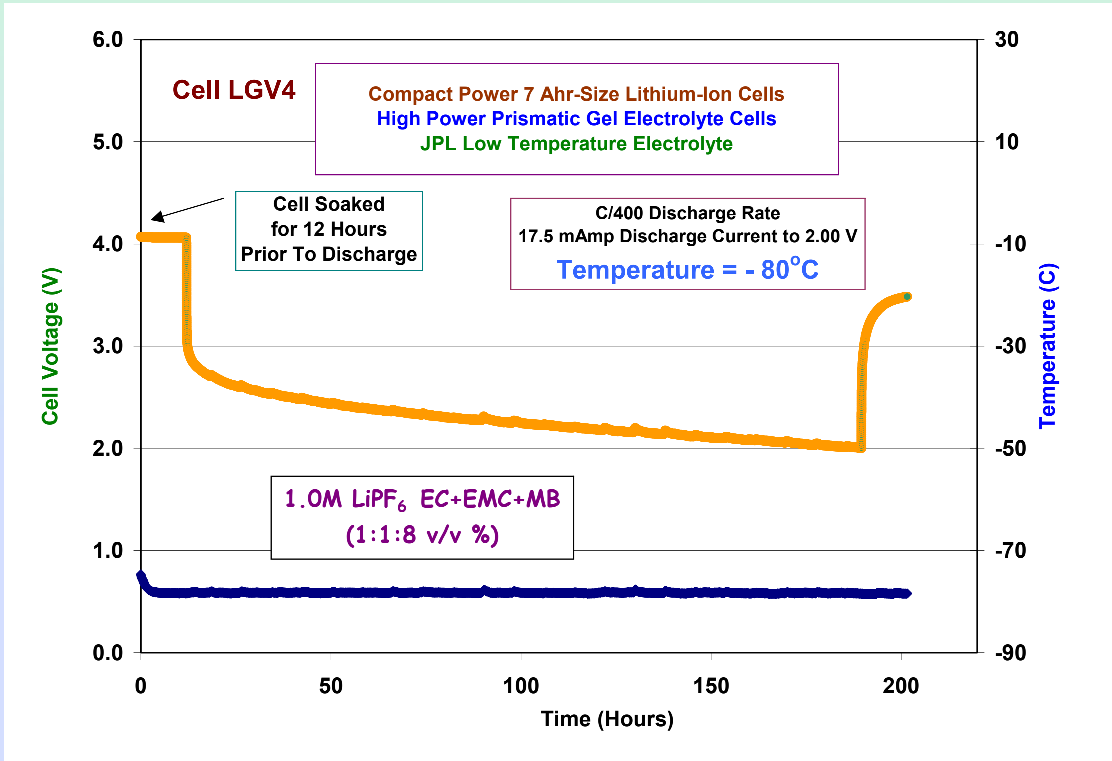
The methyl-butyrate (MB)-containing electrolyte demonstrated superior performance at –70°C and delivered over 80% of the room temperature capacity using low rates (C/100)

M. C. Smart, B. V. Ratnakumar, A. Behar, L.D. Whitcanack, J.-S. Yu, M. Alamgir, "Gel Polymer Electrolyte Lithium-Ion Cells with Improved Low Temperature Performance", *J. Power Sources*, **165 (2)**, 535-543 (2007).

Performance Testing of High Rate, Gel Polymer Electrolyte Li-Ion Cells

Performance of Ester-Based Electrolytes at Low Temperatures

Discharge Performance at – 80°C (MB-Based Electrolyte)



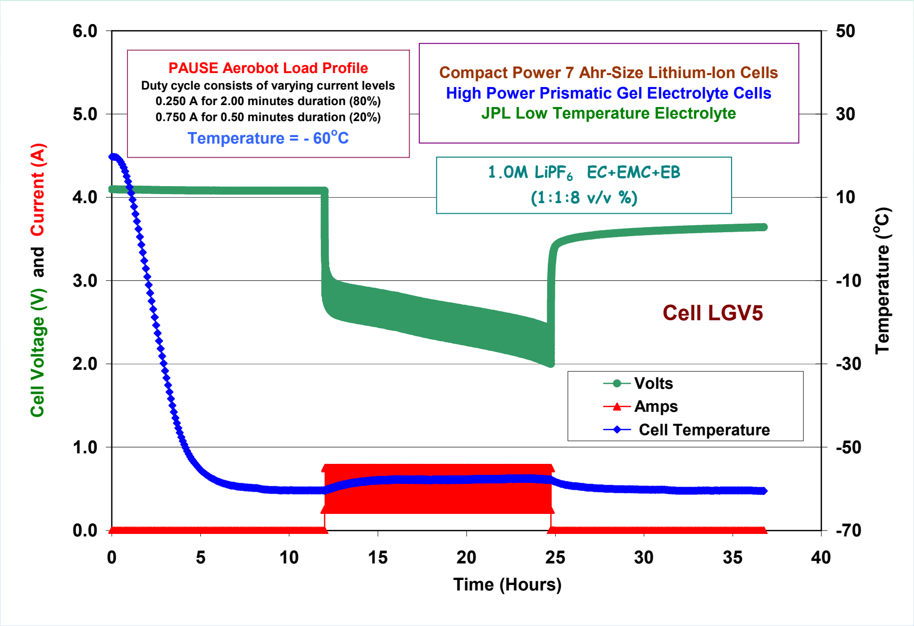
Over 175 hours of continuous operation delivered at –80°C using low rates (C/400)
Represents over 49% of the room temperature capacity,
corresponding to 3.079 Ah delivered at –80°C

M. C. Smart, B. V. Ratnakumar, A. Behar, L.D. Whitcanack, J.-S. Yu, M. Alamgir, "Gel Polymer Electrolyte Lithium-Ion Cells with Improved Low Temperature Performance", *J. Power Sources*, **165 (2)**, 535-543 (2007).

Performance Testing of High Rate, Gel Polymer Electrolyte Li-Ion Cells

Performance of Ester-Based Electrolytes at Low Temperatures

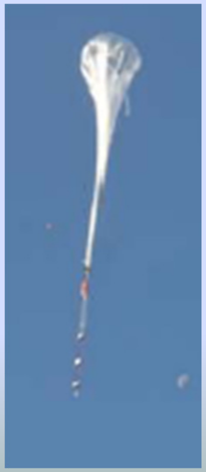
PAUSE Aerobot Load Simulation at –60°C



Investigated possibility of using low temperature Li-ion cells for the Picosat and UAV Systems Engineering (PAUSE) Project
(collaboration with Dr. Alberto Behar, JPL).

The PAUSE project utilizes a zero-pressure balloon and a prototype Mars aerobot science gondola to study the atmosphere, and is potentially subjected to very low temperatures depending upon location and altitude.

Objective is to replace the currently used Li-SO_2 primary batteries, which are unable to operate effectively below – 40°C under current load profile.



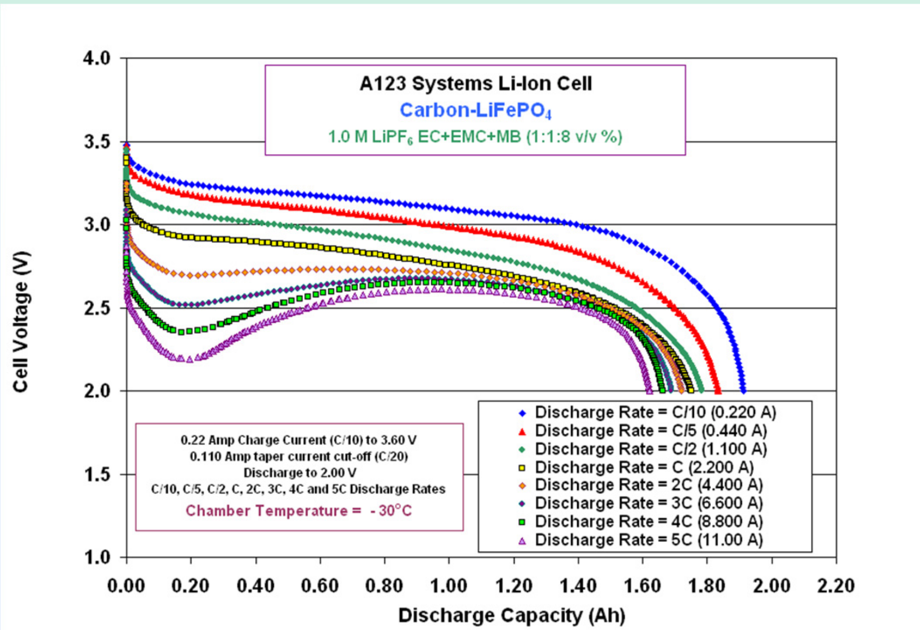
At –60°C, the high power cell containing the methyl-butyrate (MB)-containing electrolyte delivered over 12 hours of operation under PAUSE load profile.

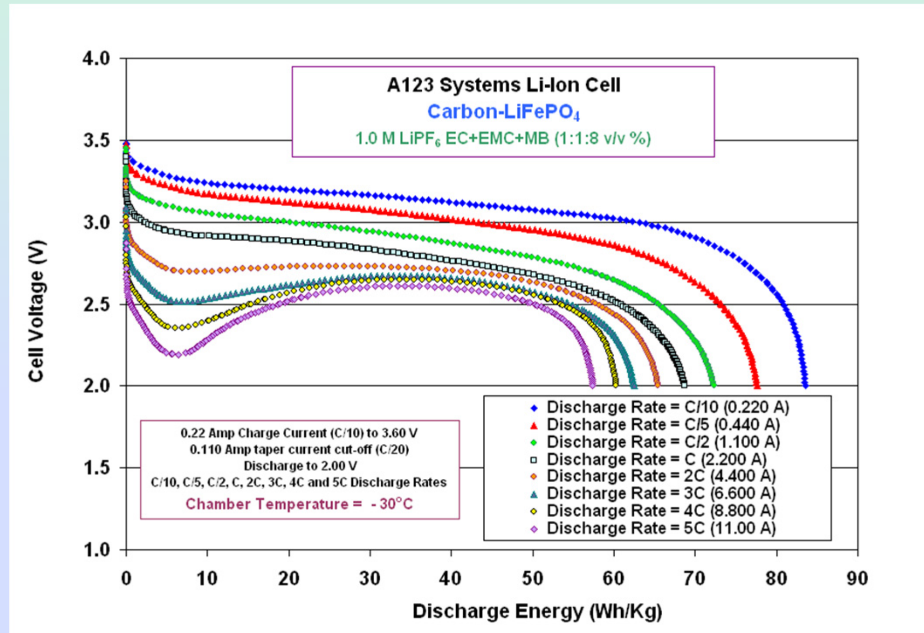
M. C. Smart, B. V. Ratnakumar, A. Behar, L.D. Whitcanack, J.-S. Yu, M. Alamgir, "Gel Polymer Electrolyte Lithium-Ion Cells with Improved Low Temperature Performance", *J. Power Sources*, **165 (2)**, 535-543 (2007).

A123 2.20 Ah High Power Lithium-Ion Cells

Discharge Rate Characterization Testing at - 30°C

Discharge Capacity (Ah) | **Discharge Energy (Wh/Kg)**





- **1.4M $LiPF_6$ in EC+EMC+MB (10:10:80)**
- **Cell both charged and discharge at -30°C**

A123 2.20 Ah High Power Lithium-Ion Cells

Discharge Rate Characterization Testing at - 60°C

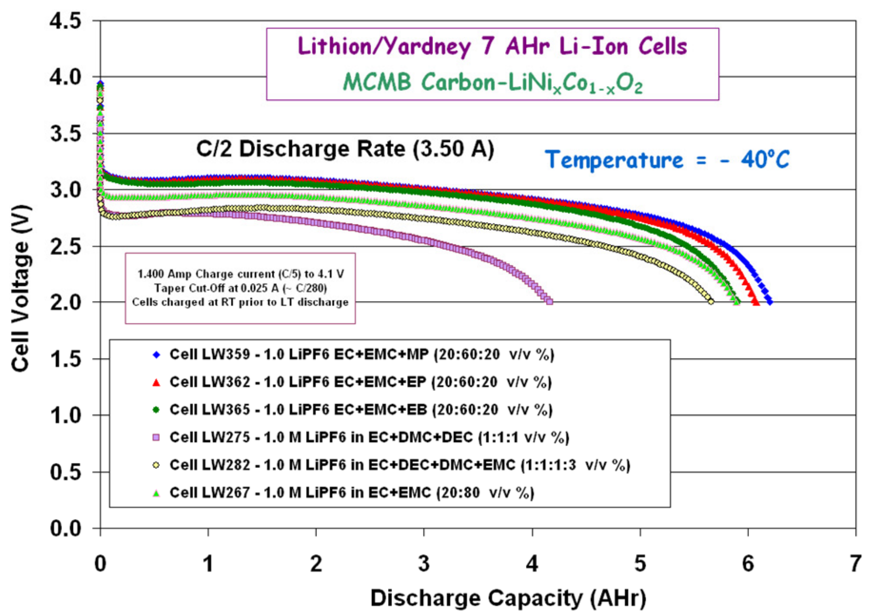
			AJ102				AJ103				AJ232				AJ233			
			1.40 M LiPF6 in EC+EMC+MB (10:10:80 v/v %)				1.40 M LiPF6 in EC+EMC+MB (10:10:80 v/v %)				A123 SSDE Control				A123 SSDE Control			
Temperature (oC)	Rate	Current (A)	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (mAh)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp
20°C (Initial)	C/5	0.400	2.3217	7.5530	107.00	100	2.2821	7.4221	106.24	100	2.4010	7.810	111.32	100	2.4093	7.839	112.02	100
- 60°C	C/2	1.100	0.0898	0.1910	2.71	3.87	0.7494	1.5624	22.37	32.84	0.0000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000
- 60°C	C/5	0.440	1.2106	2.7412	38.83	52.14	1.2578	2.8808	41.24	55.12	0.0000	0.000	0.001	0.001	0.0000	0.000	0.000	0.000
- 60°C	C/10	0.220	1.4242	3.3823	47.91	61.34	1.4210	3.3948	48.59	62.27	0.0002	0.000	0.005	0.007	0.0000	0.000	0.001	0.001
- 60°C	C/20	0.110	1.6361	4.0506	57.38	70.47	1.6078	3.9929	57.16	70.45	0.0086	0.019	0.275	0.359	0.0067	0.015	0.211	0.278
- 60°C	C/50	0.044	1.8093	4.6657	66.10	77.93	1.7726	4.5778	65.53	77.68	0.0005	0.001	0.014	0.020	0.0009	0.002	0.029	0.039
- 60°C	C/100	0.022	2.0490	5.5459	78.56	88.26	1.9891	5.3904	77.16	87.16	0.0112	0.026	0.373	0.468	0.0153	0.036	0.513	0.636

- Electrolyte = 1.4M $LiPF_6$ in EC+EMC+MB (10:10:80)
- **Over 50Wh/kg can be delivered at -60°C using a C/20 discharge rate and over 47Wh/kg with at C/10 rate.**

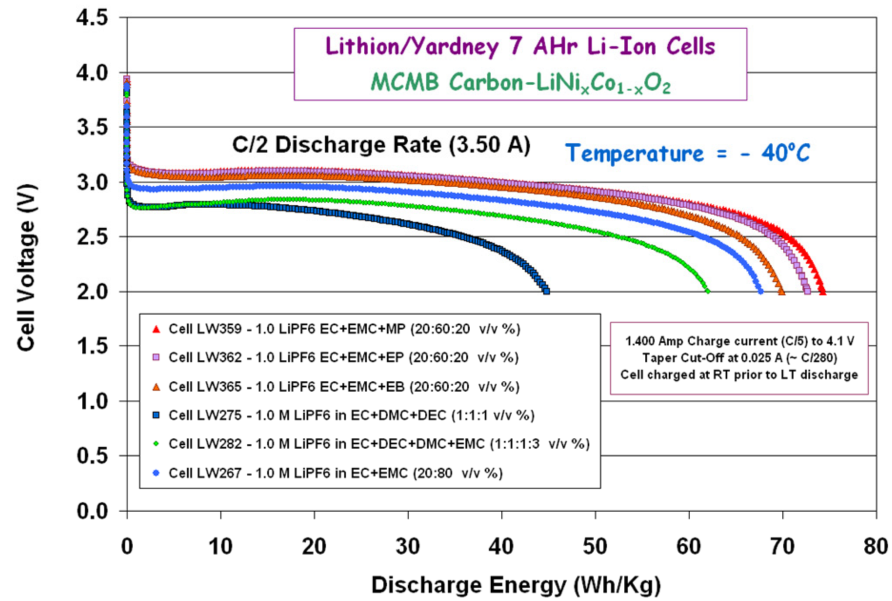
Yardney 7 Ah Prototype Cells with Advanced Electrolytes

Low Temperature Discharge Performance at -40^{o}C (C/2 Rate)

Discharge Capacity (Ah)



Discharge Energy (Wh/Kg)

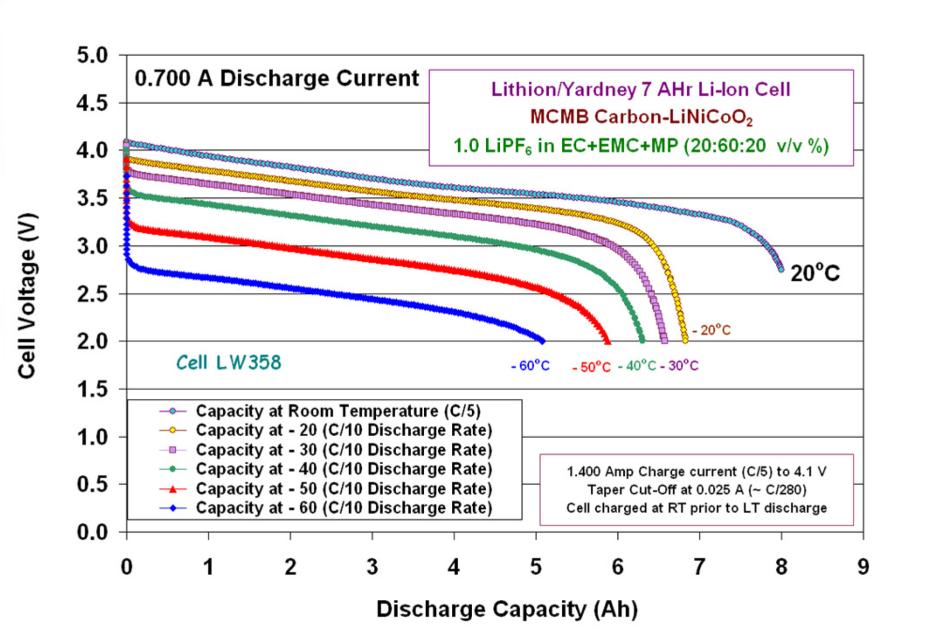


Discharge capacity (Ah) and discharge energy (Wh/Kg) at -40^{o}C, using a C/2 rate discharge (3.50 A), of prototype 7 Ah lithium-ion cells containing electrolytes consisting of 1.0M $LiPF_6$ EC+EMC+X (20:60:20 v/v %) (where X = MP, EP, and EB), as well as cells with baseline all carbonate-based electrolytes.

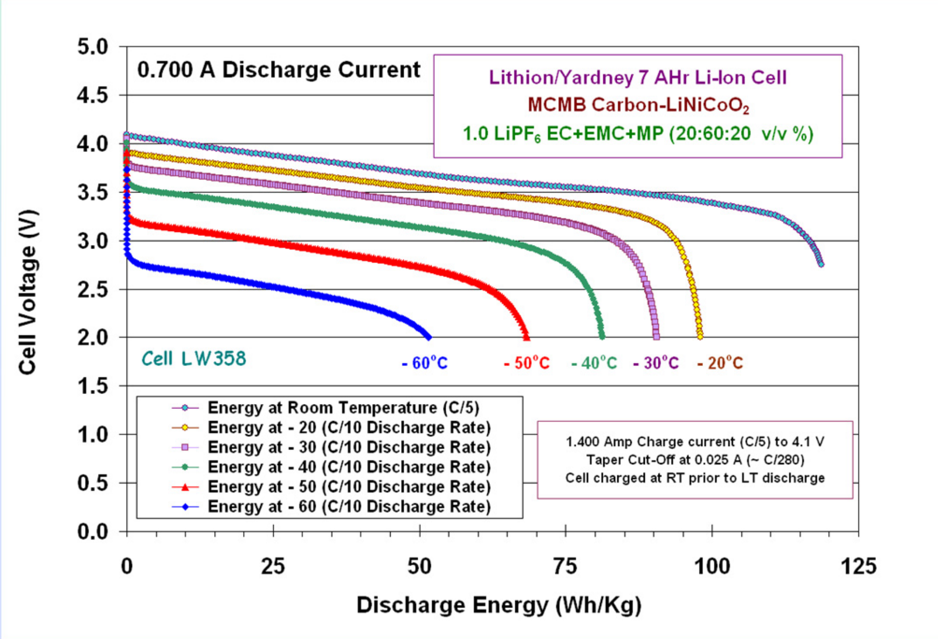
Yardney 7 Ah Prototype Cells with Advanced Electrolytes

Low Temperature Discharge Performance of Prototype Cells

Discharge Capacity (Ah)



Discharge Energy (Wh/Kg)



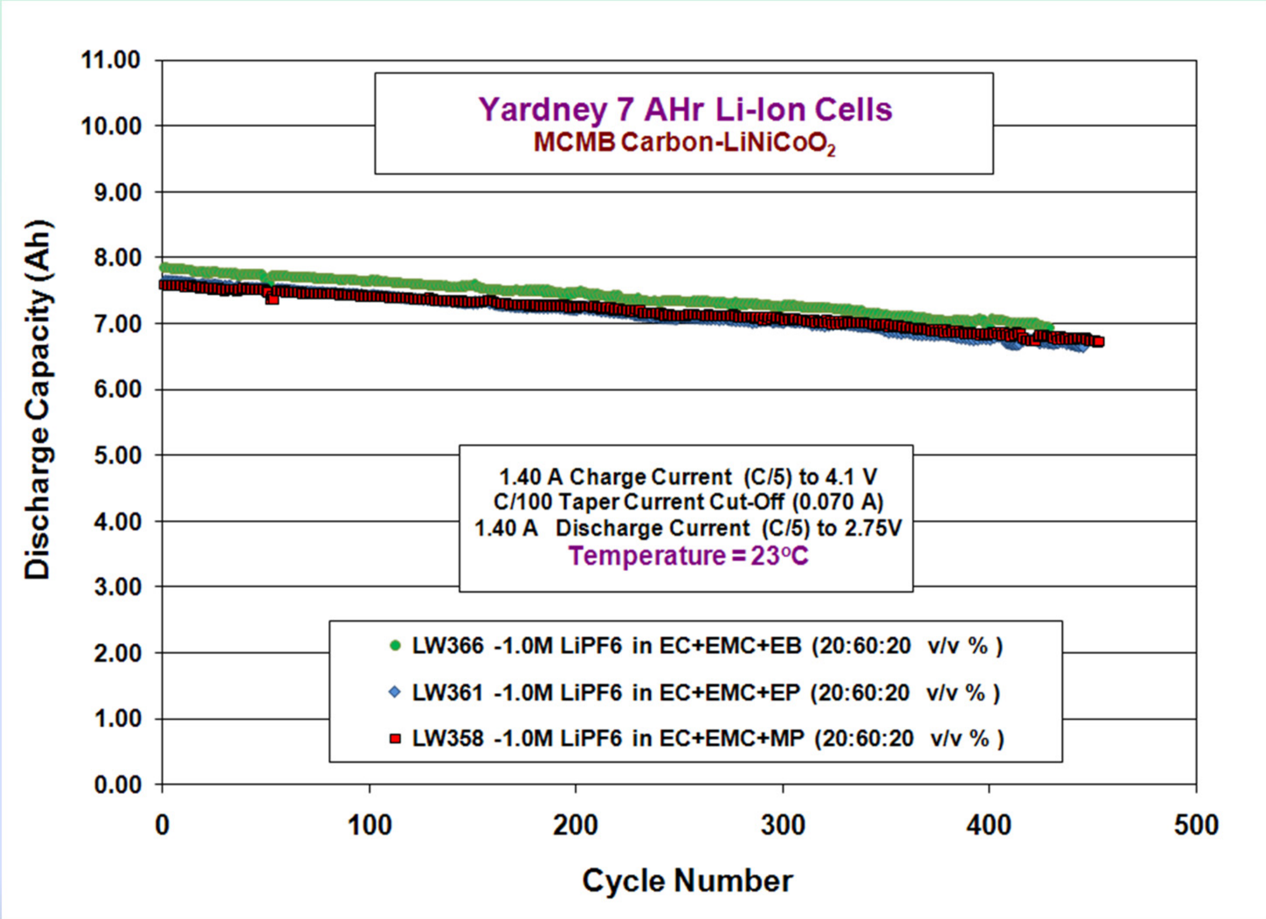
- Cells containing the methyl propionate-based electrolyte were observed to perform well down to -60°C using a C/10 discharge rate.

Yardney 7 Ah (NCP7) Prismatic Li-Ion Cells

Characterization of Cells Containing Advanced Electrolytes

100 % DOD Cycle Life Testing at Room Temperature

Discharge Capacity (Ah, %) at 20°C



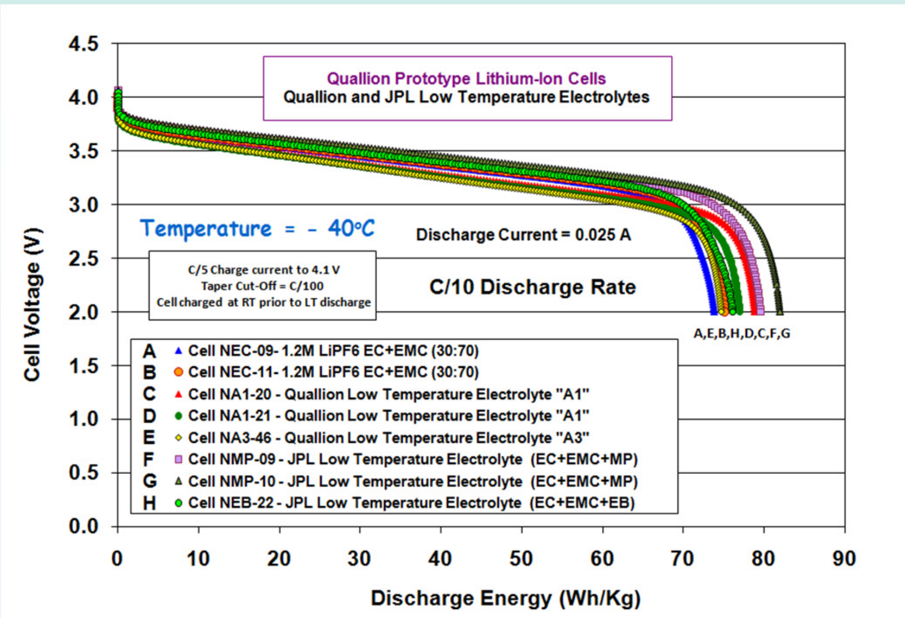
Ester-based electrolytes have been observed to display good cycle life characteristics.

Quallion Prototype Li-Ion Cells

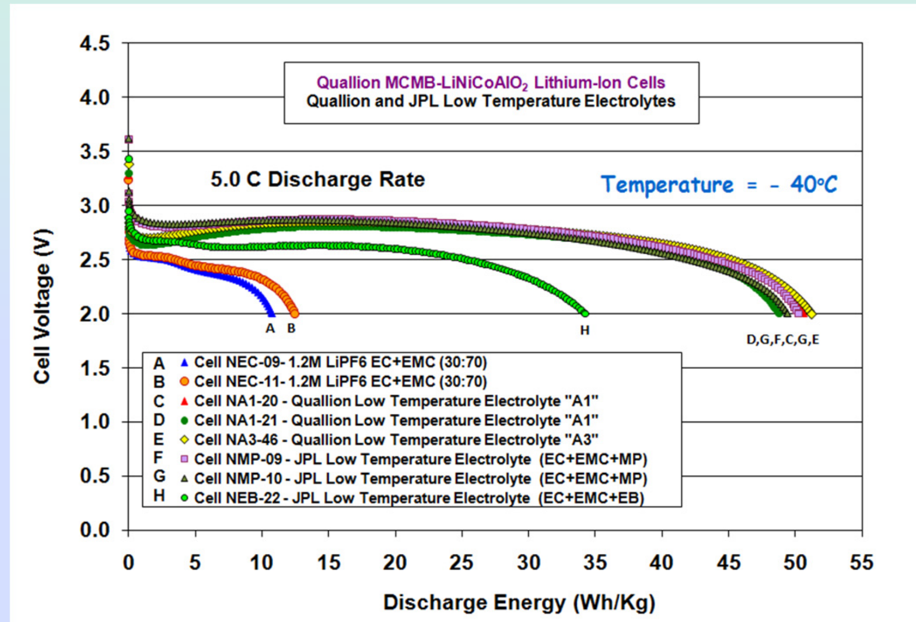
Wide Operating Temperature Electrolytes

Discharge Characterization at Various Temperatures

C/10 Discharge at -40°C



5C Discharge at -40°C !!



- In collaboration with Quallion (NASA SBIR Program), excellent low temperature rate capability has been demonstrated with advanced electrolytes.

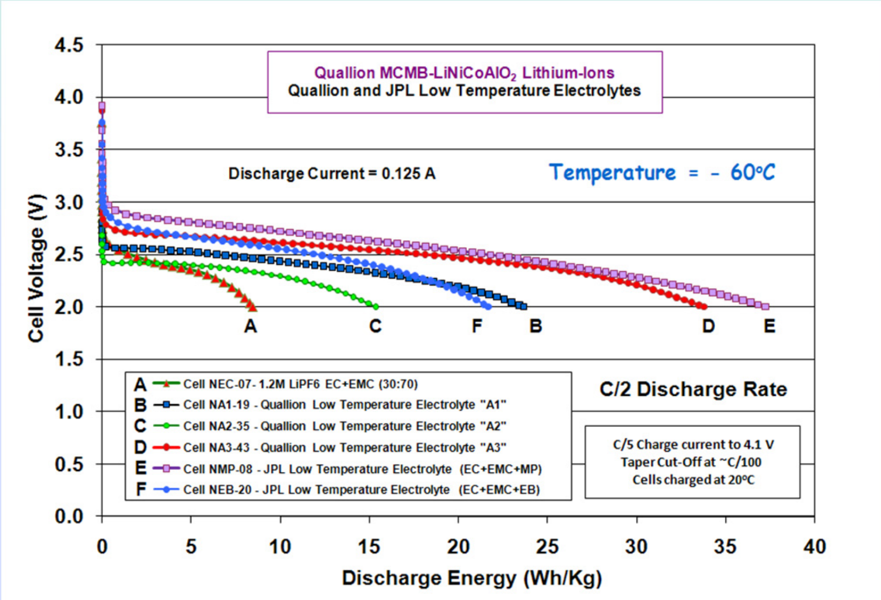
M. C. Smart, B. V. Ratnakumar, M. R. Tomcsi, M. Nagata, V. Visco, and H. Tsukamoto, "Performance of Wide Operating Temperature Range Electrolytes in Quallion Prototype Li-Ion Cells", 2010 Power Sources Conference, Las Vegas, NV, June 16, 2010.

Quallion Prototype Li-Ion Cells

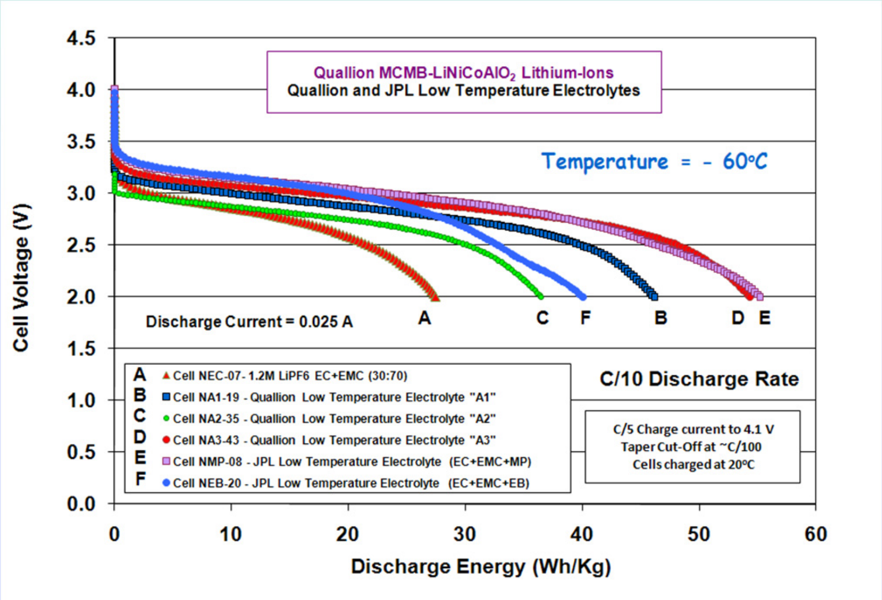
Wide Operating Temperature Electrolytes

Discharge Characterization at Various Temperatures

C/2 Discharge at -60°C (Wh/kg)



C/10 Discharge at -60°C (Wh/kg)



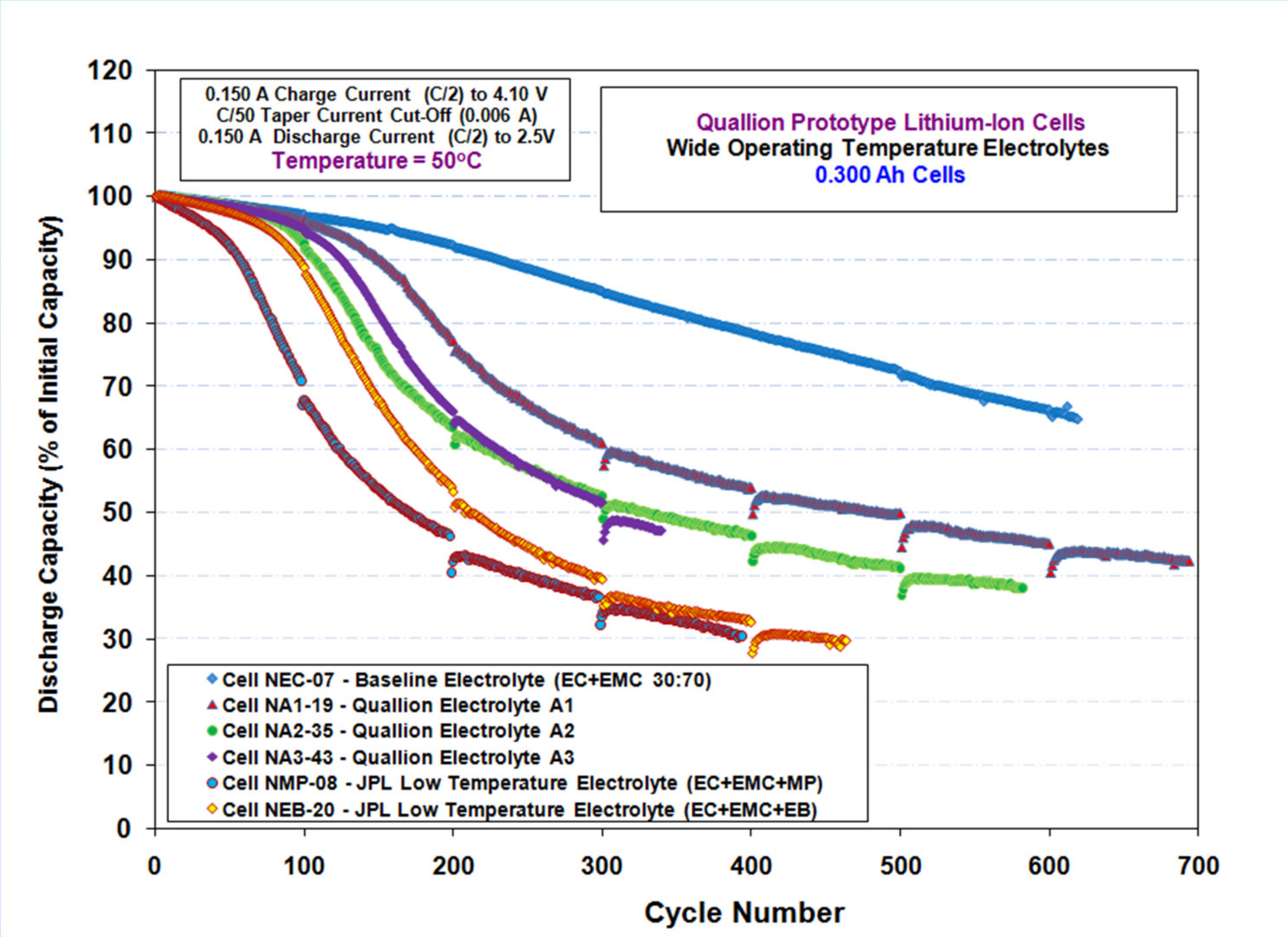
- In collaboration with Quallion (NASA SBIR Program), excellent low temperature rate capability has been demonstrated with advanced electrolytes.

M. C. Smart, B. V. Ratnakumar, M. R. Tomcsi, M. Nagata, V. Visco, and H. Tsukamoto, "Performance of Wide Operating Temperature Range Electrolytes in Quallion Prototype Li-Ion Cells", 2010 Power Sources Conference, Las Vegas, NV, June 16, 2010.

Quallion Prototype Li-Ion Cells

Wide Operating Temperature Electrolytes

Cycling at High Temperature (50°C)



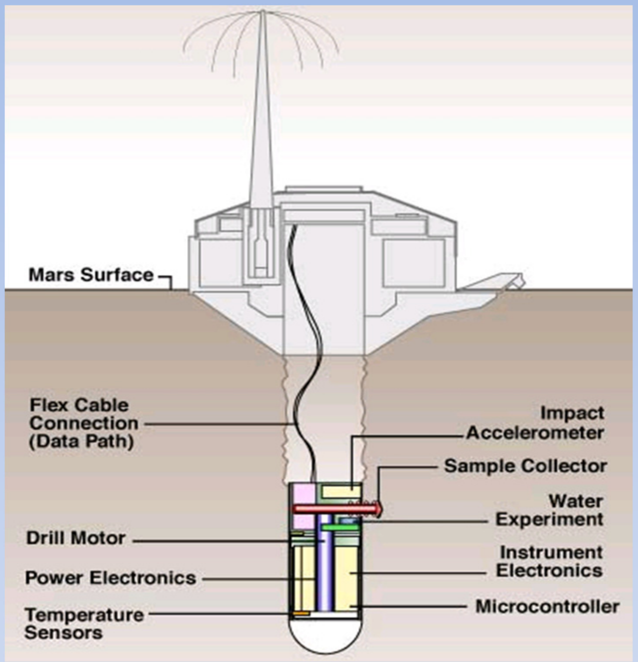
Although reasonable cycle life is observed at 50°C, the advanced wide operating temperature electrolytes display higher capacity fade compared to DOE baseline chemistry.

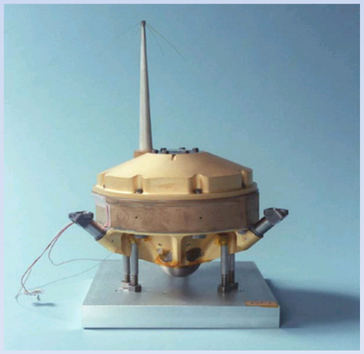
ELECTROCHEMICAL TECHNOLOGIES GROUP

Low Temperature Lithium Primary Batteries

Background: Mars DS2 Microprobe Spacecraft

- Launched on January 1999
- Two microprobes (2.4kg) piggybacked on Mars Polar Lander mission
- Intended as a low cost, high risk/high payoff mission
- Design:
  - No parachute: dropoff penetrator
  - Aftbody with batteries & telecom stays on surface
  - Forebody penetrates, ~ 1 meter
  - Drill scoops soil sample into chamber
  - Heat, vaporize, and analyze for H_2O
  - Transmit water and other science data





DS2 spacecraft

Low Temperature Lithium Primary Batteries

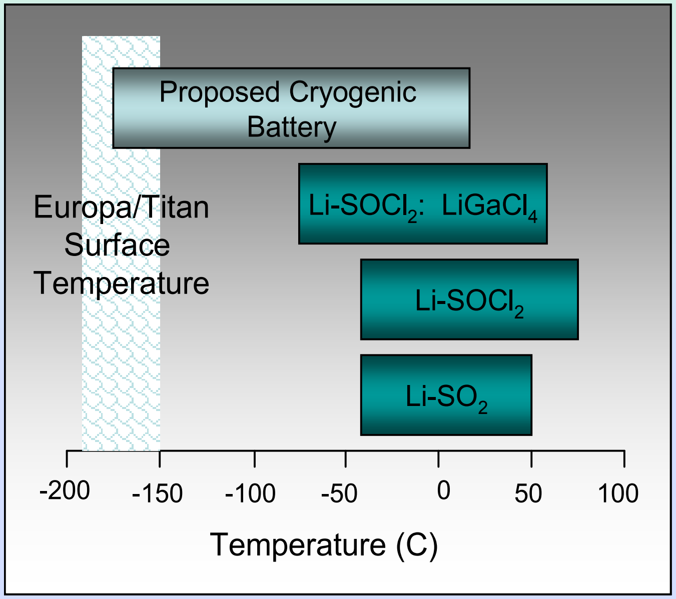
Background: Mars DS2 Battery

- Lithium-Thionyl Chloride Chemistry
  - Li anode|0.5M $LiGaCl_4$ in $SOCl_2$ catholyte|porous carbon cathode current collector
- Predicted operational temperature at nominally -80^{o}C
- "Pancake" electrode design (vertical stacking)
- Two 4 cell batteries per spacecraft
- Battery voltage: 6-14V
- Battery Capacity:
  - 550 mAhr capacity @ -80°C
  - 2 Ah at 25^{o} C
- Shelf Life: 2.5 Years
- Shock Tolerance: >80,000 g shock
- Developers/Suppliers:
  - JPL/Yardney Technical Products

DS2 lithium-thionyl chloride cells and batteries

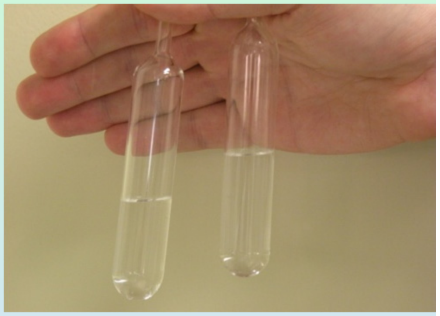
Low Temperature Lithium Primary Batteries
Motivation for New Battery Research

- How does an analogous penetrator mission to outer planetary moons (e.g. Europa, Titan) at ca. -160^{o}C draw power?
  - Maximum solar flux at Europa is only 34 W/m^2 vs. 1371 W/m^2 at low earth orbit
  - Lowest possible operating temperature for any battery is -80^{o}C
  - Heaters add undesirable power drains, mass, complexity
  - Radioisotope heaters or radioisotope thermoelectric generators are expensive and have low power density
- Proposed solution: Develop advanced catholytes with lower liquid range to infuse into existing cell design to allow for low-cost, ultra-low temperature batteries.

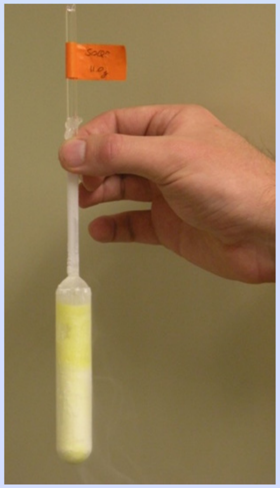


"Optimized" Catholyte System[1]

- Base catholyte: Sulfuryl chloride fluoride (SO_2ClF); m.p. -125°C, b.p. 7°C
  - SOClF disproportionates with storage, SO_2F_2 low b.p., and not likely to reduce readily by Li
- Co-solvent: chlorodifluoromethane; m.p. ($CHClF_2$); m.p. -175°C, b.p. -41°C
  - Wide range of alkanes, halocarbons, chloroethane-butylnitrile binaries examined
- Salt: $LiGaCl_4$
  - Better low temperature conductivity than $LiAlCl_4$
- Surfactant: 3 vol % of perfluoroether: Galden HT55
  - Below -120°C, 1:1 $SO_2ClF:CHClF_2$ phase separates
  - Addition of a perfluoroether suppresses the temperature of phase separation
- Halogen Passivation: Bromine (Br_2)
  - $Li-SOCl_2$ cells with BrCl, Cl_2 additives show reduced voltage delay



USC Purified SO_2ClF

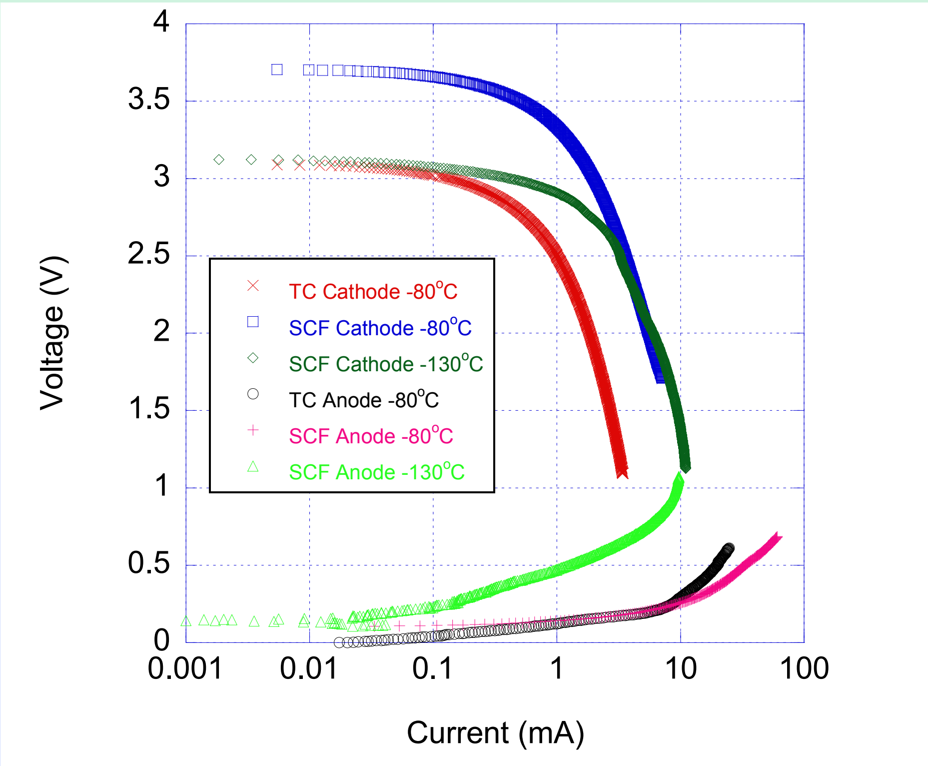


USC Synthesized SOClF

[1] W. C. West, A. Shevade, J. Soler, J. Kulleck, M. C. Smart, B. V. Ratnakumar, Matthew Moran, Ralf Haiges, and G. K. Surya Prakash, *J. Electrochem. Soc.*, **157**, A571 (2010).

Low Temperature Lithium Primary Batteries

3 Electrode Cell Study of Tafel Polarization



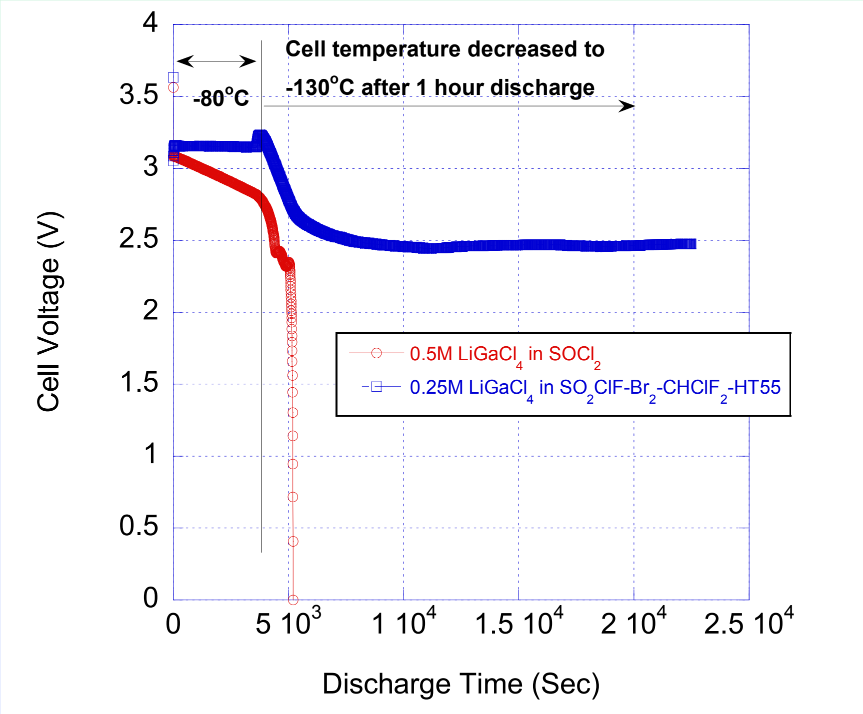
TC denotes the cell with 0.5 M $LiGaCl_4$ in $SOCl_2$ formulation and SCF denotes the cell with Br_2 passivated 0.25 M $LiGaCl_4$ in 1:1 $SO_2ClF:CHClF_2$–HT55 formulation.

- Polarization of electrodes dominated by cathode for baseline thionyl chloride and optimized low temperature formulation (non-vacuum filling issue).
- At lower temperature, the anode polarization becomes a more significant contributor to cell polarization
- Low temperature formulation at -130°C outperforms baseline formulation at -80°C

[1] W. C. West, A. Shevade, J. Soler, J. Kulleck, M. C. Smart, B. V. Ratnakumar, Matthew Moran, Ralf Haiges, and G. K. Surya Prakash, *J. Electrochem. Soc.*, **157**, A571 (2010).

Low Temperature Lithium Primary Batteries

Cell Discharge Studies

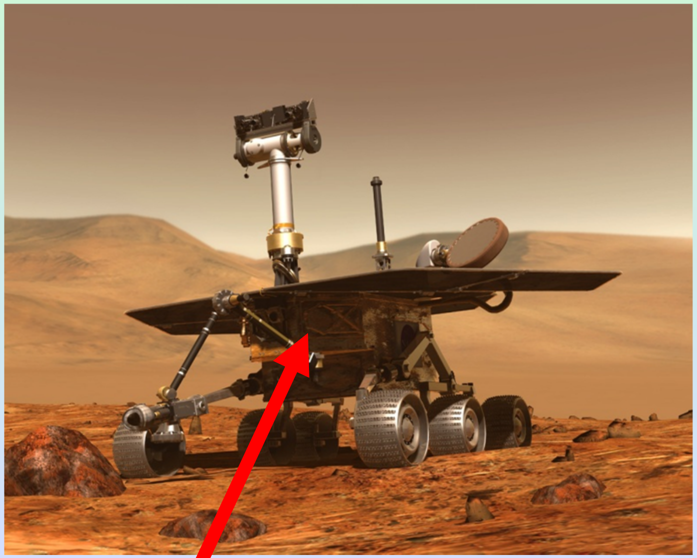


Discharge of 0.5M $LiGaCl_4$ in $SOCl_2$ cell and Br_2-passivated 0.25M $LiGaCl_4$ in 1:1 SO_2ClF:$CHClF_2$-HT55 cell. The cells were filled at -80°C, equilibrated for 1 h, discharged first at -80°C,and then cooled while discharging to -130°C.

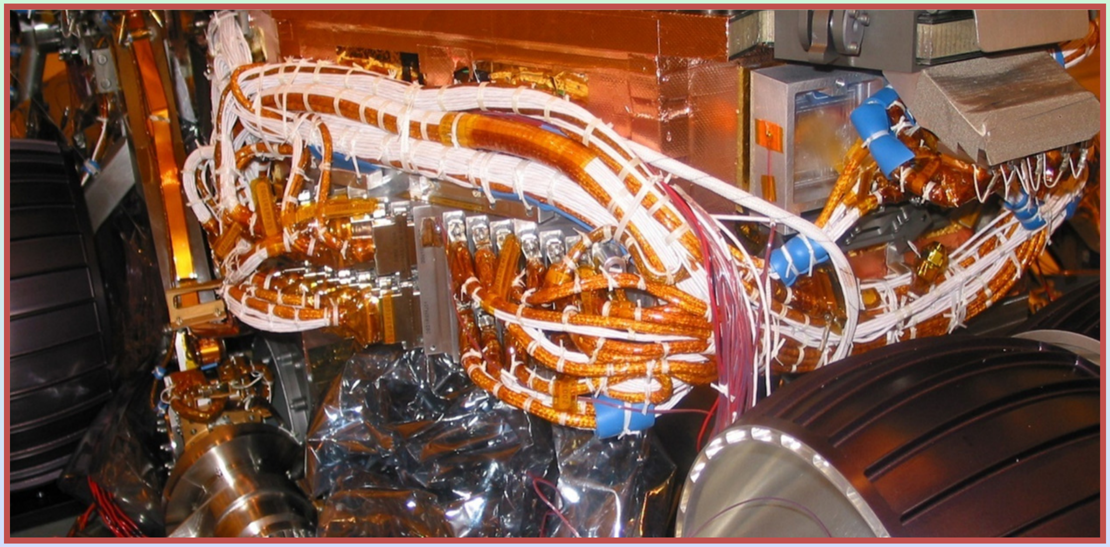
- Discharging at -80°C, low temperature formulation has flat discharge profile, unlike sloped discharge for baseline formulation.
- When temperature is reduced to -130°C, baseline formation fails as expected.
- Low temperature formulation discharges continuously with no slope in discharge profile- ***lowest operating temperature battery ever reported.***
- Lower temperatures briefly examined, may be capable as low as -145°C.

[1] W. C. West, A. Shevade, J. Soler, J. Kulleck, M. C. Smart, B. V. Ratnakumar, Matthew Moran, Ralf Haiges, and G. K. Surya Prakash, *J. Electrochem. Soc.*, **157**, A571 (2010).

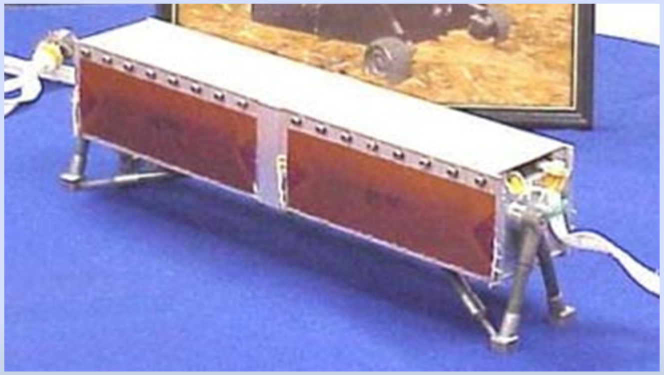
Need for low temperature power



Warm electronics box (WEB)



Cabling from the WEB



Mars Exploration Rover
Li ion battery

- **Current practice:** avionics in warm electronics box (WEB) with radioisotope heat source to maintain -40°C to +40°C
- Extensive cabling presents design, integration and test challenge
- Battery power de-rated at lower temperatures
- ***Possible solution: Hybrid low temperature battery-capacitor power systems***

Double-layer capacitors for low temperature energy storage and power delivery

Technology need

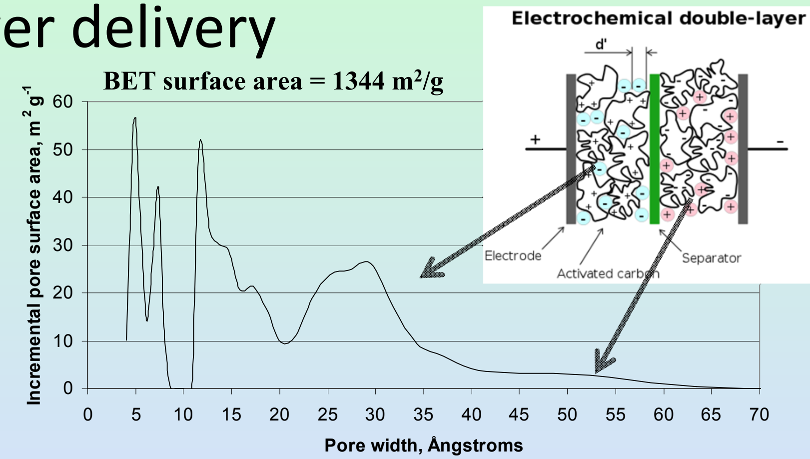
- Storing electrical energy and delivering power at low temperatures (<-30°C) remains a significant challenge
- Difficult to deliver high power effectively at low temperatures (batteries derated due to slow kinetics)

Objectives

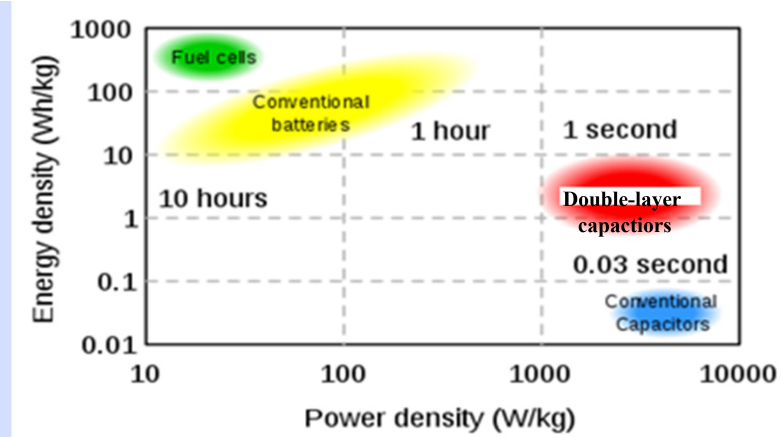
- Utilize the advantage of double-layer capacitors, which store energy *at the electrochemical double-layer* (rather than intercalation and redox processes, which are highly temperature sensitive)
- Develop low temperature electrolytes to extend beyond -40°C limit with commercial cells
- Target low equivalent series resistance (ESR) to effectively deliver power at low temperature

Potential applications

- Hybrid battery/capacitor low temperature power systems (with the capacitor providing pulse power at low temperatures)
- Capacitor-only power systems, for low duty cycle distributed sensor platforms on planetary surfaces (with limited thermal management)
- Fully testable thermal battery replacements



Incremental pore surface area vs. pore width for representative activated carbon electrode material



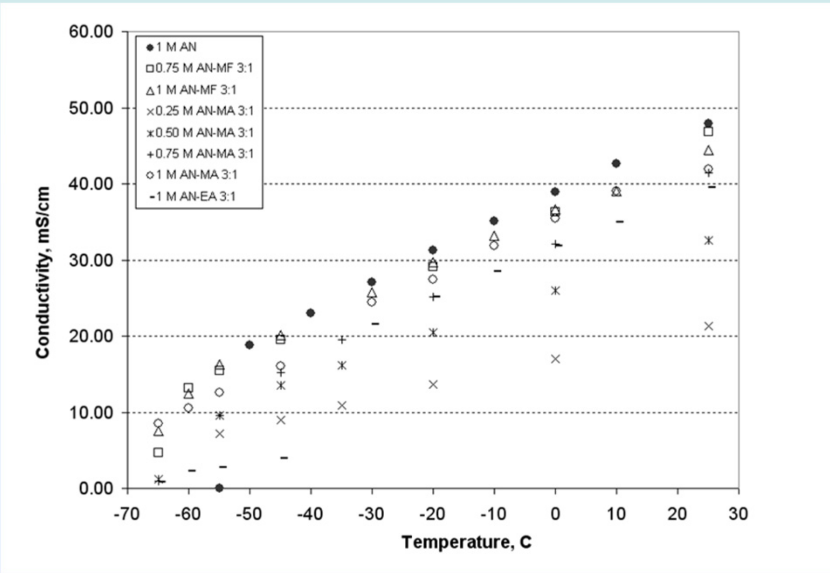
High power density/moderate energy density of double-layer capacitors can augment high energy density of batteries in low temperature power systems

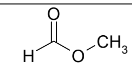
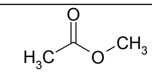
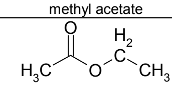
Low Temperature Supercapacitors

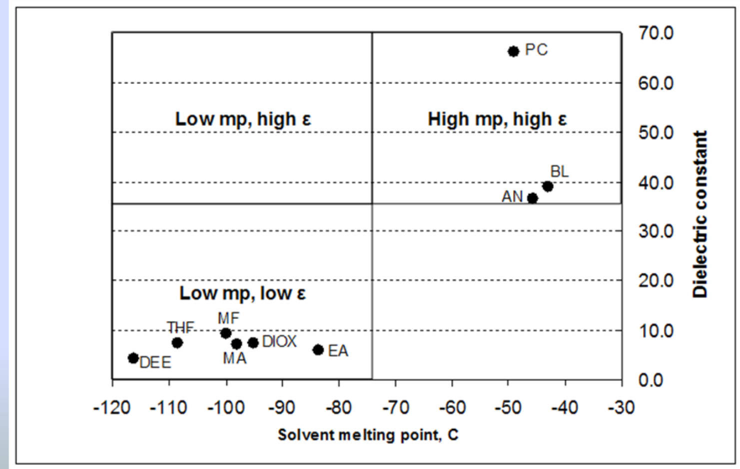
Survey of Commericially Available Technology

Technical Approach: Design non-aqueous electrolyte formulations that have high conductivity at low temperature, and much lower freezing points.

Ionic Conductivity vs. Temperature



Solvent	Freezing point (ºC)
$H_3C-C\equiv N$ acetonitrile (AN)	-43.84
 methyl formate	-100
 methyl acetate	-98
 ethyl acetate	-83.6
Acetonitrile : methyl formate (3:1 vol/vol%)	-70
Acetonitrile : methyl acetate (3:1 vol/vol%)	-71
Acetonitrile : ethyl acetate (3:1 vol/vol%)	-72



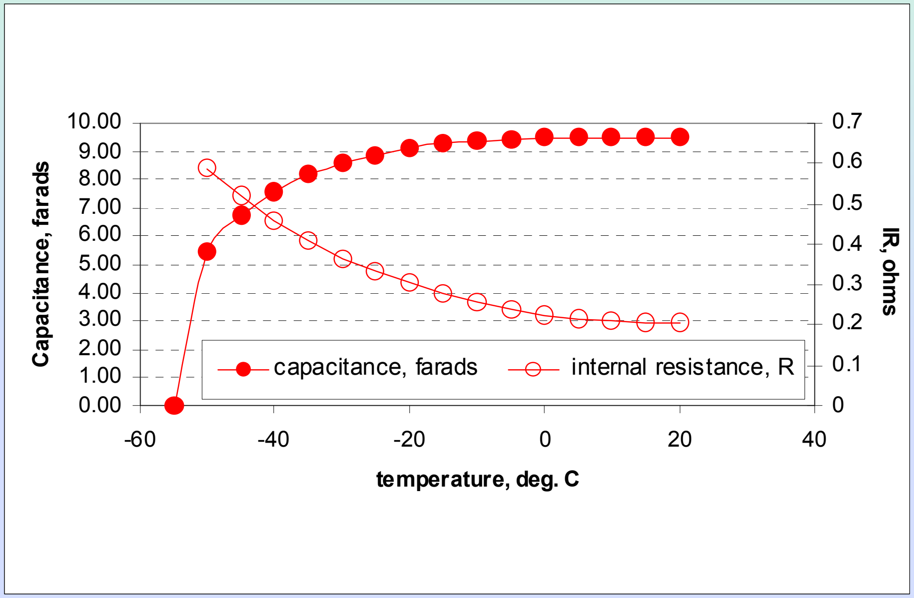
- ➢ Mixed electrolyte co-solvent blends (i.e., AN-based) were observed to provide the desired properties.

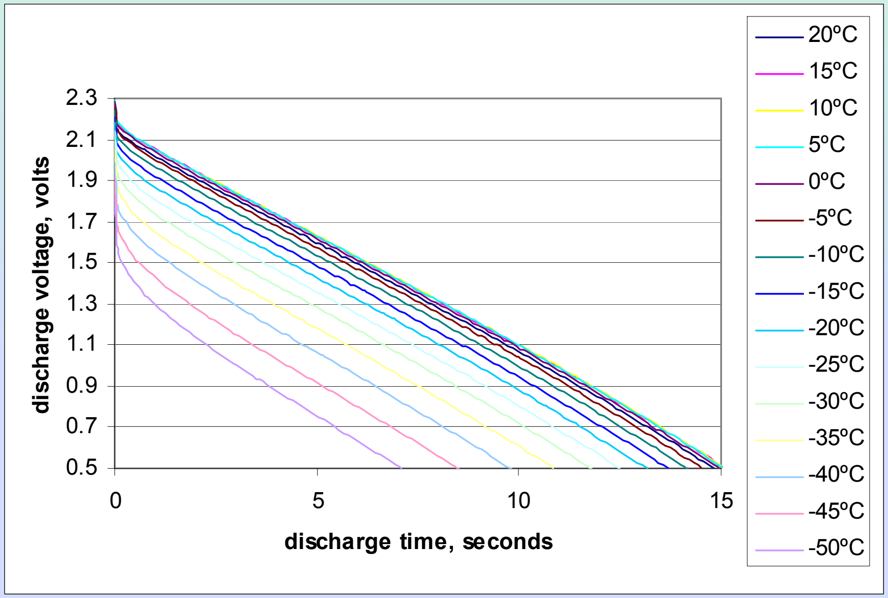
Low Temperature Supercapacitors

Survey of Commericially Available Technology

10 F cell

Discharge current = 1 A





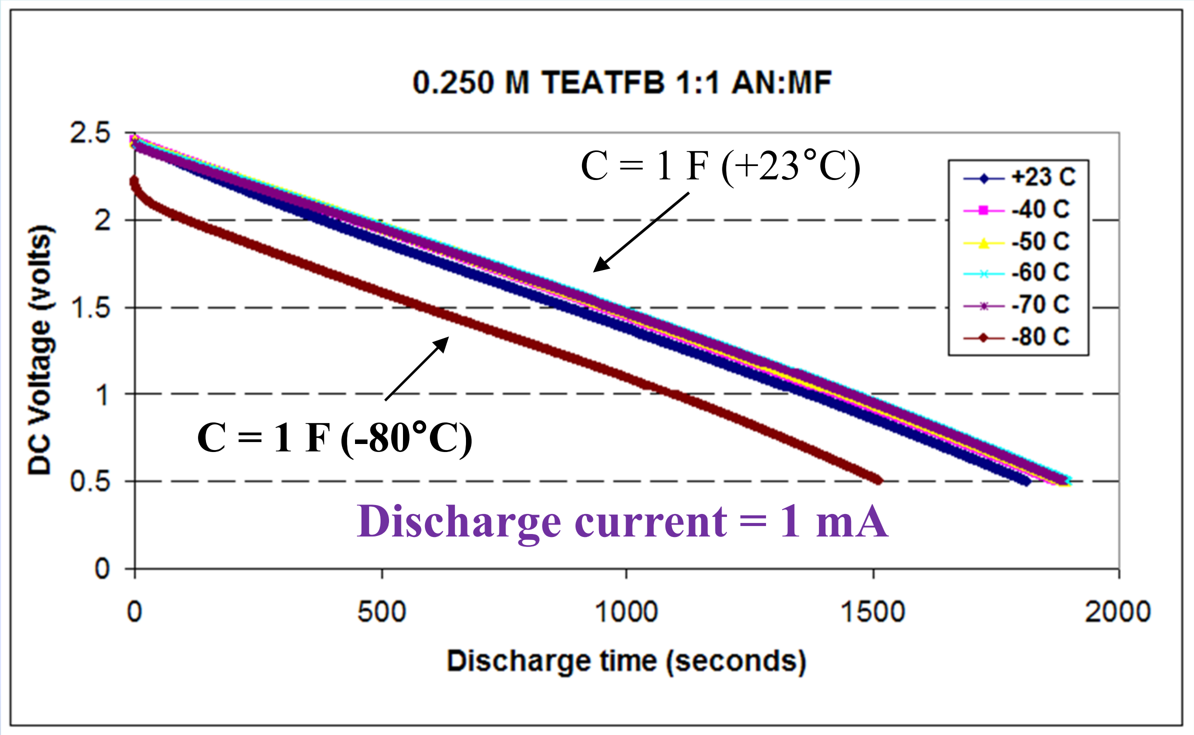
Poor performance is observed at temperatures below -50ºC

Low Temperature Supercapacitors

Advanced Low Temperature Chemistries Evaluated in Experimental Coin Cells

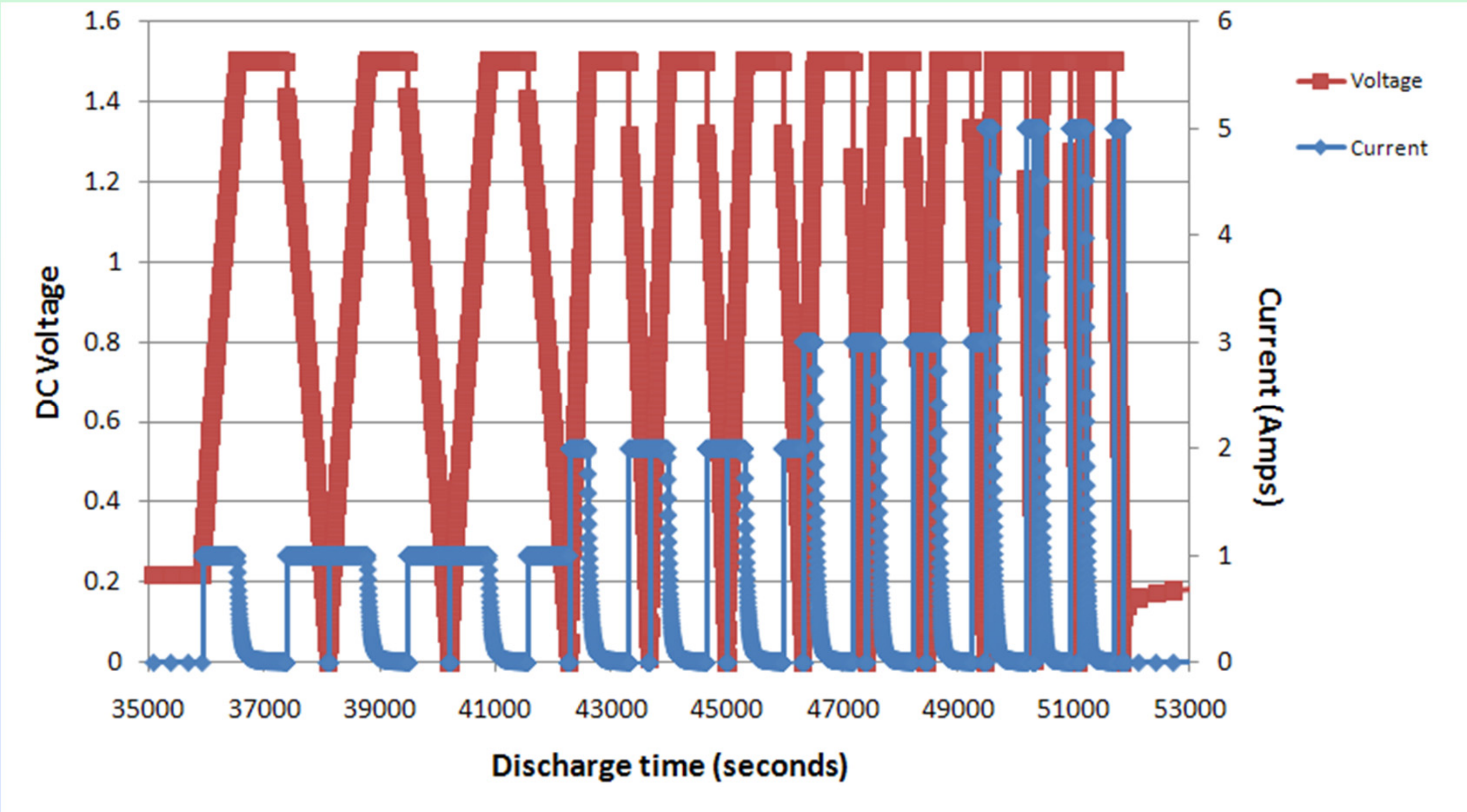
- **2032 coin cells**
- **Separator:** 25 micron polyethylene (Tonen)
- **Electrodes:** PACMM 203 activated carbon
- **Salt:** Tetraethylammonium tetrafluoroborate

Electrolyte = 0.250 M TEATFB in 1:1 acetonitrile / methyl formate



Extended operation to < -80°C as revealed by DC data

Performance of large supercapacitor cells at -70°C



At -70°C, cell displays ~520 F capacity at 1 A and Vmax = 1.5 V with very linear discharge characteristics

SUMMARY and CONCLUSIONS

- ***Demonstration of low temperature Li-ion batteries***
  - Demonstrated improved performance with wide operating temperature electrolytes containing ester co-solvents (i.e., methyl propionate and ethyl butyrate) in a number of prototype cells:
  - In Quallion cells at -40°C, the JPL developed MP-based electrolyte was demonstrated to deliver over 60% of the room temperature capacity using a 5C rate.
  - Demonstrated improved performance of Compact Power lithium-ion cells containing the ester-based low temperature electrolytes at very low temperatures (down to –80°C).
  - Demonstrated excellent rate capability at very low temperature in A123 Systems $LiFePO_4$-based lithium-ion cells containing various low temperature electrolytes (down to –60°C).
  - Demonstrated wide operating temperature range (down to –60°C) in Yardney prototype cells (7 Ah, $LiNiCoO_2$-based systems).
- ***Development of ultra-low temperature primary batteries***
  - New ultra-low temperature battery systems have been identified based on sulfuryl chloride fluoride catholytes, $LiGaCl_4$ salt, chlorofluorocarbon co-solvents, perfluoroether surfactants, and halogen passivation.
  - We report a first known demonstration of cell operation at temperatures as low as -130°C, about 60°C lower than any other battery system reported.
  - *Further studies need to be performed to incorporate the technology into commercially produced prototype cells.*
- **Development of ultra-low temperature supercapacitors**
  - Demonstrated capacitor operation to -80°C, enabled by AN-based/TEATFB formulation with the addition of low melting formates and esters.
  - Key electrolyte design factors include volume of co-solvent and electrolyte salt concentration.
  - Continuing efforts include demontrating in larger scale cells and investigating formulation targeted at lower temperatures

Acknowledgments

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA).